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Negative thermal expansion structures constructed from positive thermal expansion trusses

Teik-Cheng Lim

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Abstract The negative thermal expansivity of a type of space frame structure is investigated herein. On the basis of space frame structure consisting of tetrahedral representative volume elements, a volumetric thermal strain, and a volumetric coefficient of thermal expansion (CTE) models are developed in this article for a special category of tetrahedron that is made from two types of materials, each for the three apex and the three base rods. Based on these models, the conditions for attaining negative volumetric thermal strain and negative coefficient of volumetric thermal expansion are established. Plotted results reveal a trend in which the extent of negative expansivity is increased for lower apex-to-base rod length and CTE ratios, and higher base rod CTE.

Introduction

Heat generated in industrial machineries, aircraft structures, energy plants, and other engineering structures raises the temperature of structural materials, which is accompanied by expansion. Under geometrical constraints on thermal strains, the resulting thermal stresses add to the loading stresses of these structures. Negative thermal expansion (NTE) materials, on the other hand, shrink with elevated temperature. As such, the use of NTE materials alongside conventional or positive thermal expansion (PTE) materials helps to alleviate thermal stresses. The NTE components create space due to contraction during heating, thereby paving a way for the PTE components to expand without, or with minimal, constraints. Arising from early works on NTE polymers [1–3], a number of NTE materials have since been synthesized for investigation and/or application. Recent NTE materials cover all classes of materials [4–24]. Of special interests is the capability of materials and structures that not only exhibits NTE behavior, but also allows some extent of adjustment to the coefficient of thermal expansion (CTE) [25, 26]. These have been made possible through the use of connected triangular blocks [27, 28], multilayered system [29, 30], and composites with needle-like inclusions [31]. A 2D periodic network that consists of three sets of rods of different materials is known to produce adjustable thermal expansivity. It has been shown that triangles having one side made from a different material from the other two sides can be made to exhibit negative thermal expansion (NTE) [32–34]. A generalized study on the triangular network for various combinations of different rod lengths and different rod coefficients of thermal expansions (CTE) further supports the high adjustability of this networks thermal expansivity from negative to positive [35]. In this article a 3D periodic network consisting six sets of rods arranged in a tetrahedron, which is generally known in the structural engineering domain as space frame trusses, is explored for its NTE as an extension of the 2D network. Some combinations of rod lengths and rod CTEs that lead to overall negative CTEs to the space frame trusses are established. The use of hinged rods herein is akin to the negative compressibility and NTE studies by Fortes et al. [36] and Grima et al. [37, 38].

T.-C. Lim (✉)
School of Science and Technology, SIM University,
Singapore, Singapore
e-mail: alan_tc_lim@yahoo.com

Geometrical analysis

With reference to the 2D periodic network that consists of isosceles triangles shown in Fig. 1, it is easily seen that

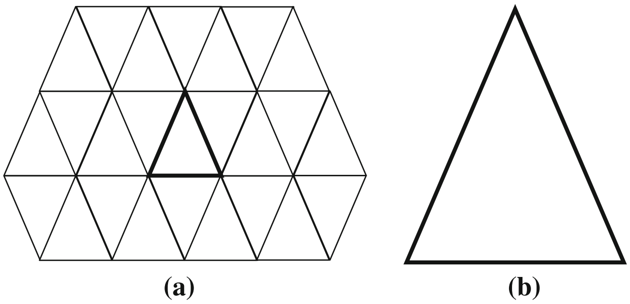

Fig. 1 A triangular periodic rod/truss structure that gives variable CTE: **a** 2D periodic structure, and **b** a representative area element

when the horizontal rod begins expanding (at fixed diagonal rod length) there is an increase in the triangular area until a maximum point is reached, whereupon further expansion of the horizontal rod is accompanied by area reduction until a state of zero area is attained when the triangle collapses into a horizontal line [32–34]. However, an increase in the length of the diagonal rods (at fixed horizontal rod length) does not lead to area reduction.

On the basis of this understanding, the 3D version is identified as a tetrahedron consisting of two sets of rods: (a) the first set of three rods of length a and CTE α_a are branched from the tetrahedron apex, while (b) the second set of three rods of length b and CTE α_b forms a triangular loop that defines the boundary of the tetrahedron base. This combination is selected due to its analogy with the 2D network mentioned, i.e., an increase in the "apex" rod length (at fixed "base" rod length) does not give any volumetric reduction. Increase in the "base" rod length (at fixed "apex" rod length) from the state of sharp tetrahedron is followed by volumetric increase. However, the same increment of base rod length in the state of flat tetrahedron is followed by volumetric decrease. A state of zero volume is finally attained when all six rods lie on the same plane (Fig. 2).

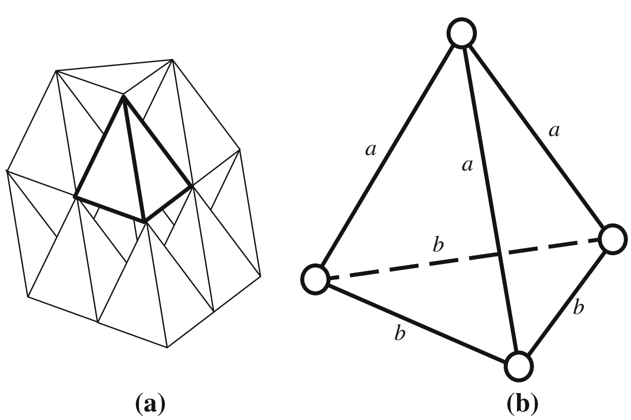

Fig. 2 A tetrahedral periodic rod/truss structure that gives variable CTE: **a** 3D periodic structure, and **b** a representative volume element

Table 1 Geometrical condition for NTE

	$\alpha_a = 0,\ \alpha_b > 0$	$\alpha_a > 0,\ \alpha_b = 0$
$\frac{a}{b} < \frac{1}{\sqrt{2}}$	NTE	PTE
$\frac{a}{b} > \frac{1}{\sqrt{2}}$	PTE	PTE

To establish the ratio of the apex-to-base rod length at the optimum point, we write the volume of the tetrahedron as

$$V = \frac{b^3}{12}\sqrt{3\left(\frac{a}{b}\right)^2 - 1} \tag{1}$$

such that the condition

$$\frac{\mathrm{d}V}{\mathrm{d}a} = 0 \tag{2}$$

has no solution, thereby confirming positive thermal expansion (PTE) of the tetrahedron when $\alpha_a > \alpha_b = 0$.

On the other hand, there is a solution for

$$\frac{\mathrm{d}V}{\mathrm{d}b} = 0 \quad \Leftrightarrow \quad \frac{a}{b} = \frac{1}{\sqrt{2}}, \tag{3}$$

thereby quantifying the earlier qualitative elucidation for $\alpha_b > \alpha_a = 0$. Table 1 summarizes the geometrical condition that leads to NTE for the scope of tetrahedral structure considered herein.

Thermal Analysis

It is known that as a solid undergoes thermal expansion from its original volume V_0 to its final volume V_f by an amount dV resulting from a temperature increment of ΔT, i.e.,

$$V_\mathrm{f} = V_0 + \mathrm{d}V, \tag{4}$$

the volumetric strain by definition is

$$\varepsilon_V = \frac{\mathrm{d}V}{V_0} \tag{5}$$

while its relationship with the coefficient of volumetric thermal expansion (CVTE), α_V is

$$\varepsilon_{VT} = \alpha_V \Delta T. \tag{6}$$

Equating both volumetric strains

$$\mathrm{d}V = \alpha_V V_0 \Delta T, \tag{7}$$

we have

$$V_\mathrm{f} = (1 + \alpha_V \Delta T) V_0. \tag{8}$$

Hence the volumetric strain resulting from thermal expansion

$$\varepsilon_{VT} = \frac{V_f}{V_0} - 1, \tag{9}$$

can be expressed in terms of the rod dimensions before and after thermal expansions, i.e.,

$$\begin{Bmatrix} V_f \\ V_0 \end{Bmatrix} = \frac{1}{12} \begin{Bmatrix} b_f^3 \sqrt{3(a_f/b_f)^2 - 1} \\ b_0^3 \sqrt{3(a_0/b_0)^2 - 1} \end{Bmatrix}. \tag{10}$$

Substituting

$$\begin{Bmatrix} a_f \\ b_f \end{Bmatrix} = \begin{Bmatrix} (1 + \alpha_a \Delta T) a_0 \\ (1 + \alpha_b \Delta T) b_0 \end{Bmatrix}, \tag{11}$$

we arrive at

$$\varepsilon_{VT} = -1 + (1 + \alpha_b \Delta T)^2 \sqrt{\frac{3\left(\frac{a_0}{b_0}\right)^2 (1 + \alpha_a \Delta T)^2 - (1 + \alpha_b \Delta T)^2}{3\left(\frac{a_0}{b_0}\right)^2 - 1}}. \tag{12}$$

It follows that, for a solid to exhibit NTE, the volumetric thermal strain must be less than zero. Hence the condition

$$(1 + \alpha_b \Delta T)^2 \sqrt{\frac{3\left(\frac{a_0}{b_0}\right)^2 (1 + \alpha_a \Delta T)^2 - (1 + \alpha_b \Delta T)^2}{3\left(\frac{a_0}{b_0}\right)^2 - 1}} < 1 \tag{13}$$

must be fulfilled for the considered space frame structure to be NTE. The CVTE can be obtained by taking the first derivative of the volumetric thermal strain with respect to the thermal increment

$$\alpha_V = \frac{d\varepsilon_{VT}}{d(\Delta T)} \tag{14}$$

to give

$$\alpha_V = 2\alpha_b (1 + \alpha_b \Delta T) \sqrt{\frac{3\left(\frac{a_0}{b_0}\right)^2 (1 + \alpha_a \Delta T)^2 - (1 + \alpha_b \Delta T)^2}{3\left(\frac{a_0}{b_0}\right)^2 - 1}} + \alpha_b (1 + \alpha_b \Delta T)^2 \frac{3\left(\frac{\alpha_a}{\alpha_b}\right)\left(\frac{a_0}{b_0}\right)^2 (1 + \alpha_a \Delta T) - (1 + \alpha_b \Delta T)}{\sqrt{3\left(\frac{a_0}{b_0}\right)^2 - 1} \times \sqrt{3\left(\frac{a_0}{b_0}\right)^2 (1 + \alpha_a \Delta T)^2 - (1 + \alpha_b \Delta T)^2}}. \tag{15}$$

Equation 15 implies that the CVTE of a structure composed of rods in tetrahedral arrangement is dependent on the magnitude of temperature change. This result is not surprising since it is understood that the structural geometry changes with changes to the rod length.

The CVTE as a material property that is independent from the change in temperature is obtained by taking the limits

$$\lim_{\Delta T \to 0} \alpha_V = \alpha_b \left(2 + \frac{3\left(\frac{\alpha_a}{\alpha_b}\right)\left(\frac{a_0}{b_0}\right)^2 - 1}{3\left(\frac{a_0}{b_0}\right)^2 - 1} \right). \tag{16}$$

Equation 16 refers to the CVTE at infinitesimal change in temperature, and is hence valid for small change in temperature. It is also valid for moderate change in temperature under the condition that the changes in the tetrahedron volume and shape are insignificant. It follows that, for the structure to possess a negative CVTE, the condition

$$\left(2 + \frac{\alpha_a}{\alpha_b}\right)\left(\frac{a_0}{b_0}\right)^2 < 1 \tag{17}$$

must be met. The next section discusses the results of variation in volumetric thermal strain and volumetric CTE with reference to a dimensionless rod CTE and the rod ratio, respectively.

Results and discussion

Figure 3 shows variation of the volumetric thermal strain with reference to a dimensionless rod CTE, $\alpha_b \Delta T$, under various rod length ratios. This parameter $\alpha_b \Delta T$ was selected over $\alpha_a \Delta T$ due to the role that the "base" rods play in giving rise to NTE. The effect of the "apex" rods' CTE is taken into consideration on Fig. 3a–c whereby $\alpha_a/\alpha_b =$ 0.0, 0.1, and 0.2, respectively.

Perusal to Fig. 3 shows that the extent of negative expansivity becomes more significant with

(a) decreasing rod length ratio a_0/b_0,
(b) increasing dimensionless rod CTE, $\alpha_b \Delta T$, and
(c) decreasing rod CTE ratio α_a/α_b.

In addition to the above, it can be seen that under the condition where there is a slight PTE, the overall volumetric thermal expansion goes into a negative region beyond certain increase in temperature, hence temperature change dependent NTE.

Figure 4a shows general variation of the infinitesimal volumetric CTE with reference to the rod length ratio, under various ratio of base rod CTE to apex rod CTE. Owing to the close variation in the curves, an appreciation on the influence of rod length ratio and rod CTE ratio is made in Fig. 4b, c, which zoomed in on a narrow range of

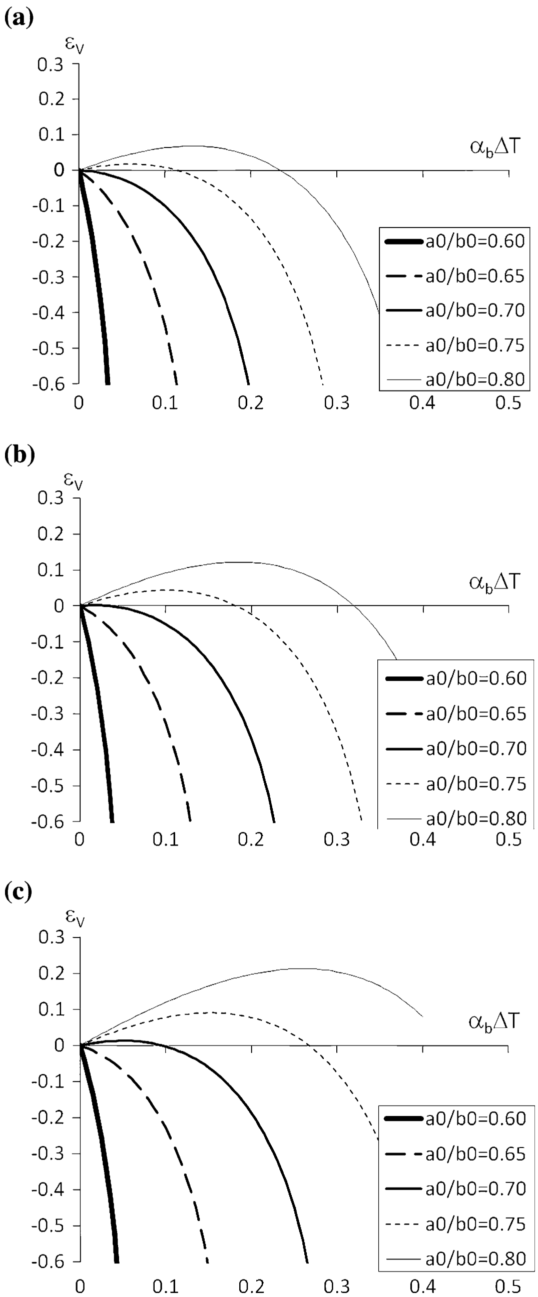

Fig. 3 Plots of volumetric thermal expansion versus dimensionless rod CTE for various rod ratios at: **a** $\alpha_a/\alpha_b = 0.0$, **b** $\alpha_a/\alpha_b = 0.1$, and **c** $\alpha_a/\alpha_b = 0.2$

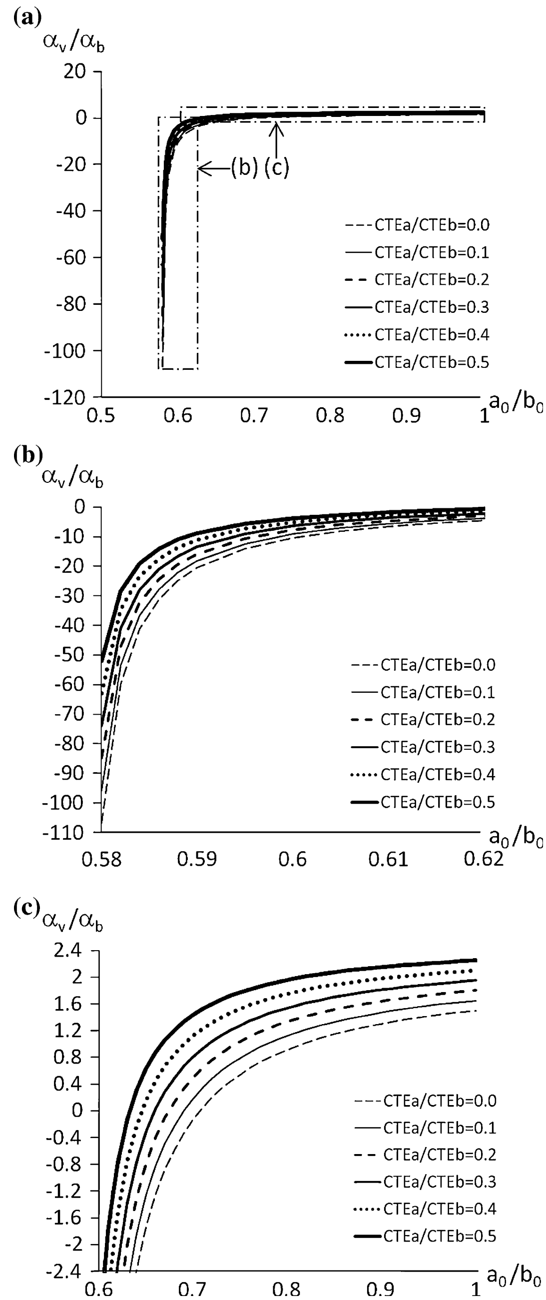

Fig. 4 Plots of dimensionless volumetric CTE versus rod ratio for various rod CTE ratios: **a** general trend, **b** zoomed in view at rod ratio of 0.6 ± 0.02, and **c** zoomed in view at dimensionless volumetric CTE range of $-2.4 \leq (\alpha_V/\alpha_b) \leq 2.4$

rod length ratio and a narrow range of dimensionless volumetric CTE.

As with Fig. 3, reference to Fig. 4 reveals that the degree of negative expansivity is more pronounced with decreasing rod length ratio a_0/b_0 and rod CTE ratio α_a/α_b. More striking, however, is that the extent of negative expansivity increases gradually with decreasing rod ratio for $a_0/b_0 > 0.6$, but the negative expansivity increases sharply with decreasing rod ratio for $a_0/b_0 < 0.6$. This may well be attributed to the limiting geometrical condition, in which the minimum limit for the rod ratio is $a_0/b_0 = 3^{-0.5} = 0.57735$.

Many materials that exhibit NTE owe their characteristic to specific geometrical arrangement and rotation of rigid units (e.g., tetrahedral, octahedral, etc.,) of elements in covalent bonds, such as ZrW_2O_8 [39] and ZrV2O7 [40, 41]. A high NTE rod has been found in the case of

O–Cu–O linkage in $CuScO_2$ by Li et al. [42]. Unlike the discovery by Li et al. [42], this article describes a non-rigid tetrahedral structure with non-negative thermal expansion in each link. A material design for such NTE solid can be achieved by replacing the hinged rods with chemical bonds, in which the lower CTE in the apex rods and the higher CTE in the base rods refer to chemical bonds of high stiffness and low stiffness, respectively. Density functional theory (DFT) simulation by Goodwin et al. [43] showed that silver(I) hexacyanocobaltate(III), $Ag_3[Co(CN)_6]$ possess PTE and NTE of very high magnitude. DFT calculation by Goodwin et al. [43] revealed that the magnitude of NTE is 14 times larger than in ZrW_2O_8. An example of deformable tetrahedral structure considered in this article can be seen in the case whereby the apex rods are made from $C-C \equiv C-C$ while the base rods are made of $C-O-H \cdots O{=}C$ such that each of the end carbon atom forms four bonds in tetrahedral configuration. Hence the fully covalent link in the apex rod and the partial covalent link separated by hydrogen bond in the base rod give rise to high and low bond stiffness, respectively. This leads to low and high CTE in the apex and base rods, respectively. In addition, the apex link $C-C \equiv C-C$ is shorter than the base link $C-O-H \cdots O{=}C$. Approximating these conditions as $\alpha_a = 0$, $\alpha_b > 0$ and $(a/b) < (1/\sqrt{2})$, the requirements of volumetric NTE is achieved as shown in Table 1.

Conclusions and recommendations

The thermal expansivity of a space frame structure consisting of tetrahedral units has been considered herein, with special attention to negative thermal expansivity. A model for the temperature-dependent volumetric thermal strain and a model for the volumetric thermal CTE for infinitesimal change in temperature have been developed for a special case whereby the tetrahedral unit consists of two types rod materials, in which each type has similar rod length. The conditions for negative volumetric thermal strain and for negative coefficient of volumetric thermal expansion have been established in terms of the original rod lengths and the individual rod CTEs. Results reveal that a negative thermal expansion is more likely for the considered space frame structure if the apex-to-base rod length ratio and CTE ratio are lower and the dimensionless base rod CTE is higher. A more generalized formulation of the tetrahedral CTE is suggested for future analysis.

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