

# Comment on “Negative Thermal Expansion in Single-Component Systems with Isotropic Interactions”

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Negative thermal expansion is usually observed in non-close-packed systems with directional interactions (e.g., ice,<sup>1</sup> graphene,<sup>2</sup> etc.) and complex compounds (e.g., Cu<sub>2</sub>O,<sup>3</sup> ZrW<sub>2</sub>O<sub>8</sub>,<sup>4</sup> β-quartz,<sup>5</sup> some zeolites,<sup>6</sup> etc.). However, in a paper by Rechtsman, Stillinger, and Torquato,<sup>7</sup> it was shown that negative thermal expansion (NTE) is also realized in single-component close-packed lattices with pair central force interactions. The pair potential giving rise to this behavior was derived. The main idea used for the derivation is that “a sufficient condition for a potential to give rise to a system with NTE behavior is that it exhibits a softened interior core within a basin of attraction”. Mathematically “softened interior core” means a positive third derivative of interatomic potential at the equilibrium. In the present Comment it is shown that this condition is (i) necessary and sufficient in a one-dimensional case and (ii) sufficient, but not necessary, in two and three dimensions. It is demonstrated that in the multidimensional case NTE is realized even when the third derivative of the potential is zero or negative.

In the present Comment, the sign of volumetric thermal expansion coefficient  $\alpha$  is investigated using the well-known relation between  $\alpha$  and Grüneisen parameter  $\Gamma$ :

$$\alpha = \frac{\Gamma \rho c_V}{K_T} \quad (1)$$

where  $\rho$  is density,  $c_V$  is the principal heat at constant volume,  $K_T$  is the isothermal bulk modulus. Because  $\rho$ ,  $c_V$ , and  $K_T$  are positive, then  $\alpha$  and  $\Gamma$  have the same sign. Therefore, analysis of the relation between Grüneisen parameter and interatomic potential yields the condition required for NTE. For simplicity all derivations are carried out at zero cold pressure.

First, consider one-dimensional chain with pair potential interactions. Grüneisen parameter for the unstretched chain has the form (see, e.g., ref 8):

$$\Gamma = -\frac{\Pi'''(a)a}{2\Pi''(a)} \quad (2)$$

where  $\Pi$  is the interatomic potential and  $a$  is the equilibrium distance. Formulas 1 and 2 yield the condition for NTE in the one-dimensional case

$$\Pi'''(a) > 0 \quad (3)$$

Thus, in the one-dimensional case, condition 3, proposed in the original paper<sup>7</sup> is necessary and sufficient for negative thermal expansion.

Consider simple example demonstrating that in two and three dimensions condition 3 is not necessary. Assume that

interactions between particles are harmonic; i.e., the interatomic potential is a quadratic function of the distance. Stacey<sup>9,10</sup> has shown both analytically and numerically that thermal expansion of harmonic lattice is negative. Therefore, condition 3 is not necessary.

To derive necessary and sufficient condition the exact relation between Grüneisen parameter and parameters of interatomic potential is required. Unfortunately, to our knowledge, it is not present in the literature. An approximate expression for Grüneisen parameter of undeformed simple close-packed lattice with pair force interactions in  $N$ -dimensional case is<sup>11,12</sup>

$$\Gamma = -\frac{\Pi'''(a)a + (N-1)\Pi''(a)}{2N\Pi''(a)} \quad (4)$$

Note the qualitative difference between one-dimensional and multidimensional cases. In one-dimensional case the thermal expansion is caused by the anharmonicity of the interatomic potential only. Therefore, the sign of the thermal expansion coefficient is determined by the sign of the third derivative of the potential. In the multidimensional case, the geometrical nonlinearity is also present; i.e., lattice vibrations are nonlinear even in the case of harmonic interatomic potential. This nonlinearity contributes to thermal expansion (see, e.g., ref 9). Therefore, in the multidimensional case both  $\Pi''$  and  $\Pi'''$  are present in the condition for negative thermal expansion that follows from eq 4:

$$\Pi'''(a)a > -(N-1)\Pi''(a) \quad (5)$$

The value in the right-hand side is negative for  $N > 1$ . Then in the multidimensional case negative thermal expansion is realized even when the third derivative of the potential is zero or negative. Therefore, the class of pair potentials giving rise to negative thermal expansion is significantly wider than one derived in a paper by Rechtsman, Stillinger, and Torquato.<sup>7</sup>

One may argue that formula 4 is approximate and therefore the given conclusion is too strong. However, the analysis carried out in ref 13 shows that the inaccuracy of formula 4 may not qualitatively change inequality 5.

Thus, inequality 5 can be considered as an *approximate* necessary and sufficient condition for negative thermal expansion in close-packed systems with pair central force interactions. Formulation of the *exact* condition still remains a

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challenge. The present Comment is intended to encourage future work in this direction.

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### Notes

The authors declare no competing financial interest.

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