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Nonlinear positive/negative thermal expansion and equations of state of a chain with longitudinal and transverse vibrations

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Thermal expansion of a classical chain with pair interactions performing longitudinal and transverse vibrations is investigated. Corresponding equations of state are derived analytically using series expansions of pressure and thermal energy with respect to deformations of the bonds caused by thermal motion. In the first approximation the equation of state has Mie–Grüneisen form. The dependence of Grüneisen parameter on deformation of the chain is obtained. For Lennard-Jones-like potential Grüneisen parameter varies with deformation from minus infinity (at zero stretching) to plus infinity (at the breakage point). Necessary and sufficient condition for negative thermal expansion at low thermal energies is formulated. Using this condition the potential giving rise to negative thermal expansion in the

given range of deformations can be designed. It is shown that at small deformations and finite thermal energies Mie–Grüneisen equation of state strongly overestimates the absolute value of pressure. More accurate nonlinear equation of state is derived for this case. The equation implies that thermal pressure in the unstretched chain is proportional to *square root* of thermal energy. In the vicinity of the deformation, corresponding to zero Grüneisen parameter, the chain demonstrates negative thermal expansion at low temperatures and positive thermal expansion at higher temperatures. This phenomenon is qualitatively described by the nonlinear equation of state derived in the present paper. The theoretical findings are supported by the results of molecular dynamics simulations.

1 Introduction The majority of materials have positive thermal expansion coefficient, i.e., expand upon heating. However, a certain class of materials demonstrates negative thermal expansion (NTE). For example, ice has negative thermal expansion at low temperatures [1]. Another well-known example is graphene [2]. Many other natural and synthetic materials demonstrating NTE are listed in review papers [3–6]. Since these materials have a great potential in a variety of applications, it is important to investigate physical mechanisms underlining NTE. The mechanisms include transverse vibrations of atoms [6–8, 16], rigid-unit modes [5, 9–11] and some others. Intuitively the mechanisms are well-understood. However accurate prediction of the relation between thermal expansion and microscopic

properties of a material (chemical composition, lattice structure, interatomic potential, etc.) is still a challenging problem. This issue is usually addressed by using methods of statistical physics [12]. Theoretically all thermodynamic properties of a solid can be obtained if the partition function is known. However, the calculation of the partition function involves calculation of complicated integral over N-dimensional phase space. The integral can be calculated exactly only in the so-called quasi-harmonic approximation [13] or for very simple one-dimensional models [14]. In many cases the quasiharmonic approximation is insufficient. In particular it cannot describe the dependence of thermal expansion coefficient on temperature. Many attempts to take into account unharmonic effects in the framework of statistical physics approach have been

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made in literature (see e.g., recent papers [15–17]). However, the problem of accounting for anharmonicity is still far from being solved.

An alternative approach is based on series expansion of pressure and thermal energy with respect to small parameter characterizing thermal motion [19, 18, 20]. The approach was successfully used in one, two, and three dimensions for derivation of equations of state describing thermal expansion in perfect crystals. The expression for Grüneisen parameter of close-packed crystals with pair interactions was derived [18, 20]. An approximate necessary and sufficient condition for a pair potential that give rise to NTE was formulated [21]. In the present paper, this approach is used for investigation of thermal expansion in a chain with longitudinal and transverse vibrations. In a recent paper, [16] it is shown using similar model that transverse vibrations are responsible for thermal expansion in a wide class of ceramic and hybrid materials. Also the chain can be considered, for example, as the simplest model of a nanowire [22].

In the present paper, it is shown analytically and numerically that the chain with longitudinal and transverse vibrations demonstrates very reach thermal expansion behavior. At small thermal energies the chain has positive, zero, or negative thermal expansion coefficient depending on deformation. At some values of deformation the thermal expansion coefficient of the chain is *infinite*. The nonlinear equation of state describing this and other phenomena is derived. Analytical findings are supported by results of molecular dynamics simulations.

2 Micro- and macro parameters of the model
Consider longitudinal and transverse vibrations of an infinite chain consisting of interacting particles. In the absence of thermal motion the particles are equally spaced along the straight line. At finite temperatures the particles vibrate around their average positions. Compressive deformations of the chain are not considered. It is assumed that thermal motion is sufficiently small so that the chain does not break. Only interactions between the nearest neighbors are taken into account. The steady state of the system is investigated. In this case average characteristics associated with all particles are identical. Therefore only "reference" particle with the nearest neighbors is considered below. The neighbors are marked by indexes 1 and -1. Vector connecting the reference particle with particle 1 is represented as $\mathbf{A} + \widetilde{\mathbf{A}}$, where $\mathbf{A} = A\mathbf{e}$, A is an average distance between neighbors, $\mathbf{e}$ is a vector collinear with the chain at zero thermal motion, $\widetilde{\mathbf{A}}$ is a variation of vector connecting particles due to the thermal motion. By the definition the averaged vector $\widetilde{\mathbf{A}}$ is equal to zero. The particles interact via pair potential $\varPi\left((\mathbf{A} + \widetilde{\mathbf{A}})^2\right)$. It is assumed that the potential can be expanded into a power series. The rate of convergence of the series determines the accuracy and applicability range for equations of state derived below (see Eqs. (5) and (16)). The equation of motion

of the reference particle has the form

$$m\dot{\mathbf{v}} = \mathbf{F}_1 + \mathbf{F}_{-1}, \quad \mathbf{F}_1 = 2\varPi'\left((\mathbf{A} + \widetilde{\mathbf{A}})^2\right)\left(\mathbf{A} + \widetilde{\mathbf{A}}\right),$$
(1)

where $\mathbf{F}_1$ and $\mathbf{F}_{-1}$ are the forces acting on the reference particles due to neighbors 1 and -1, respectively. Here and below a prime denotes the derivative with respect to argument of the function.

Macroscopic constitutive parameters of the system are defined as follows. The total pressure p is equal to the average force acting on the reference particle in the direction of the chain given by vector $\mathbf{e}$. It is decomposed into cold p_0 and thermal p_T contributions:

$$p = -\langle \mathbf{F}_1 \rangle \cdot \mathbf{e}, \quad p_0 = -2\varPi'(A^2)A, \quad p_T = p - p_0.$$
(2)

The thermal energy E_T is represented as a sum of kinetic K_T and potential U_T contributions:

$$E_T = K_T + U_T, \quad K_T = \frac{m}{2}\langle \widetilde{\mathbf{v}}^2 \rangle,$$
$$U_T = \left\langle \varPi\left((\mathbf{A} + \widetilde{\mathbf{A}})^2\right) \right\rangle - \varPi(A^2).$$
(3)

Formulas (2) and (3) imply that the thermal pressure and thermal potential energy depend on vector $\widetilde{\mathbf{A}}$. Kinetic energy is represented in a similar form using Virial transformation (see, e.g., paper [20]):

$$K_T = \frac{1}{2}\left\langle \widetilde{\mathbf{A}} \cdot \mathbf{F}_1\left(\mathbf{A} + \widetilde{\mathbf{A}}\right) \right\rangle.$$
(4)

Thus thermal pressure p_T and thermal energy E_T depend on vector $\widetilde{\mathbf{A}}$. In the following sections $|\widetilde{\mathbf{A}}|/A$ is considered as a small parameter. Series expansion of p_T and E_T with respect to this parameter yields equations of state.

3 Linear negative/positive thermal expansion at small thermal energies
Assume that deformations of the bonds caused by thermal motion of the particles are small, i.e., $|\widetilde{\mathbf{A}}| \ll A$. Then thermal pressure (2), potential energy (3), and kinetic energy (4) can be expanded into series with respect to vector $\widetilde{\mathbf{A}}$. Leaving terms up to the second order yields:

$$K_T = U_T = \left(\varPi'\mathbf{E} + 2\varPi''A^2\mathbf{ee}\right)\cdot\cdot\left\langle \widetilde{\mathbf{A}}\widetilde{\mathbf{A}} \right\rangle,$$
$$p_T = -2\left[\varPi''A\left(\mathbf{E} + 2\mathbf{ee}\right) + 2\varPi'''A^3\mathbf{ee}\right]\cdot\cdot\left\langle \widetilde{\mathbf{A}}\widetilde{\mathbf{A}} \right\rangle,$$
(5)

where $\mathbf{e} = \mathbf{A}/A$, $\mathbf{E}$ is a two-dimensional unit tensor. Formulas (5) show that in the first approximation the thermal energy and the thermal pressure are proportional to tensor $\left\langle \widetilde{\mathbf{A}}\widetilde{\mathbf{A}} \right\rangle$

describing deformations of the bonds caused by thermal motion. Contributions of longitudinal and transverse deformations are separated as follows:

$$\widetilde{\mathbf{A}} = \alpha \mathbf{e} + \beta \mathbf{n},$$

$$\left\langle \widetilde{\mathbf{A}}\widetilde{\mathbf{A}} \right\rangle = \left\langle \alpha^2 \right\rangle \mathbf{ee} + \left\langle \beta^2 \right\rangle \mathbf{nn} + \left\langle \alpha\beta \right\rangle (\mathbf{en} + \mathbf{ne}),$$

$$(6)$$

where $\mathbf{n}$ is a unit normal to the direction of the chain; $\left\langle \alpha^2 \right\rangle$, $\left\langle \beta^2 \right\rangle$ are dispersions of longitudinal and transverse deformations of the bond respectively; $\left\langle \alpha\beta \right\rangle$ is a correlation between longitudinal and transverse deformations. From Eqs. (5) and (6) it follows that the thermal pressure and the thermal energy depend on parameters $\left\langle \alpha^2 \right\rangle$, $\left\langle \beta^2 \right\rangle$ describing thermal motion:

$$\begin{cases} p_T = -2 \left(3\Pi'' + 2\Pi''' A^2 \right) A \left\langle \alpha^2 \right\rangle - 2\Pi'' A \left\langle \beta^2 \right\rangle, \\ E_T = 2(\Pi' + 2\Pi'' A^2) \left\langle \alpha^2 \right\rangle + 2\Pi' \left\langle \beta^2 \right\rangle. \end{cases}$$

$$(7)$$

In the given approximation correlations between longitudinal and transverse vibrations $\left\langle \alpha\beta \right\rangle$ do not contribute to p_T and E_T.

To obtain the equation of state in a closed form additional relations between parameters $\left\langle \alpha^2 \right\rangle$, $\left\langle \beta^2 \right\rangle$ are required. The relations are derived using the equipartition theorem [12]. According to the theorem, kinetic energies of longitudinal and transverse vibrations are equal. Consider tensor $\left\langle \widetilde{\mathbf{v}}\widetilde{\mathbf{v}} \right\rangle$ using the following generalization of formula (4):

$$\frac{m}{2} \left\langle \widetilde{\mathbf{v}}\widetilde{\mathbf{v}} \right\rangle = \frac{1}{2} \left\langle \widetilde{\mathbf{A}}\mathbf{F}_1 \right\rangle \approx \Pi' \left\langle \widetilde{\mathbf{A}}\widetilde{\mathbf{A}} \right\rangle + 2\Pi'' \mathbf{AA} \cdot \left\langle \widetilde{\mathbf{A}}\widetilde{\mathbf{A}} \right\rangle.$$

$$(8)$$

For simplicity of further derivations, introduce the function $\hat{\Pi}$:

$$\hat{\Pi}(A) = \Pi(A^2), \quad \Pi' = \frac{\hat{\Pi}'}{2A}, \quad \Pi'' = \frac{\hat{\Pi}'' A - \hat{\Pi}'}{4A^3},$$

$$\Pi''' = \frac{\hat{\Pi}''' A^2 - 3\hat{\Pi}'' A + 3\hat{\Pi}'}{8A^5}.$$

$$(9)$$

Here the prime denotes the derivative with respect to argument of the function. Then the equipartition theorem yields the relation between dispersions of longitudinal and transverse vibrations $\left\langle \alpha^2 \right\rangle$ and $\left\langle \beta^2 \right\rangle$:

$$\frac{m}{2} \left\langle (\widetilde{\mathbf{v}} \cdot \mathbf{e})^2 \right\rangle = \frac{m}{2} \left\langle (\widetilde{\mathbf{v}} \cdot \mathbf{n})^2 \right\rangle \Rightarrow \hat{\Pi}'' \left\langle \alpha^2 \right\rangle = \frac{\hat{\Pi}'}{A} \left\langle \beta^2 \right\rangle.$$

$$(10)$$

Coefficients $\hat{\Pi}''$, $\hat{\Pi}'/A$ are equal to longitudinal and transverse stiffnesses of the chain respectively. Note that for small deformations of the chain $\hat{\Pi}'' > \hat{\Pi}'/A$. Therefore in this case the dispersion of transverse vibrations $\left\langle \beta^2 \right\rangle$ is larger than the

dispersion of longitudinal vibrations $\left\langle \alpha^2 \right\rangle$. This fact is used in the following section for derivation of nonlinear equation of state.

Excluding $\left\langle \alpha^2 \right\rangle$ and $\left\langle \beta^2 \right\rangle$ form the system of equations (7) using the relations (9) and (10) yields the equation of state in Mie–Grüneisen form:

$$p = p_0 + \frac{\Gamma(A)}{A} E_T, \quad \Gamma = \frac{\Gamma_1 + \Gamma_{\text{tr}}}{2},$$

$$\Gamma_1 = -\frac{\hat{\Pi}''' A}{2\hat{\Pi}''}, \quad \Gamma_{\text{tr}} = -\frac{\hat{\Pi}'' A - \hat{\Pi}'}{2\hat{\Pi}'}.$$

$$(11)$$

Grüneisen parameter Γ has two contributions Γ_1, Γ_{tr} from longitudinal and transverse vibrations, respectively. The contribution of longitudinal vibrations Γ_1 is caused by anharmonicity of the interatomic potential only. It vanishes in the case of harmonic potential ($\hat{\Pi}''' = 0$). In contrast, the contribution of transverse vibrations Γ_{tr} does not depend on anharmonic properties of the potential. It is caused by geometrical nonlinearity.

Formula (11) yields necessary and sufficient condition for negative thermal expansion in the chain with longitudinal and transverse vibration at low thermal energies:

$$\Gamma < 0 \quad \Leftrightarrow \quad \hat{\Pi}''' \hat{\Pi}' A + \hat{\Pi}'' \left(\hat{\Pi}'' A - \hat{\Pi}' \right) > 0. \quad (12)$$

Using formula (12) the potential giving rise to negative thermal expansion in the given range of deformations of the chain can be designed.

To illustrate the dependence of Grüneisen parameter on deformation, consider Lennard-Jones potential:

$$\hat{\Pi}(A) = \varepsilon_0 \left[\left(\frac{a}{A} \right)^{12} - 2 \left(\frac{a}{A} \right)^6 \right],$$

$$(13)$$

where ε_0 is a bond energy, a is an equilibrium distance. The dependence of Grüneisen parameter on deformation of the chain calculated using formula (11) is shown in Fig. 1. The contribution of longitudinal vibrations to the thermal pressure is positive and tends to infinity near the breakage point $b = (13/7)^{1/6}a \approx 1.109a$. The latter fact is emphasized for the one-dimensional chain in paper [19]. The contribution of transverse vibrations to the pressure is negative almost everywhere except for the small interval $A \in [1.098a; b]$. Grüneisen parameter of the unstretched chain ($A = a$) is equal to minus infinity, since $\hat{\Pi}'(a) = 0$. Zero thermal expansion is realized at the point $A = A_*$:

$$\Gamma(A_*) = 0 \quad \Leftrightarrow \quad \hat{\Pi}''' \hat{\Pi}' A_* + \hat{\Pi}'' \left(\hat{\Pi}'' A_* - \hat{\Pi}' \right) = 0.$$

$$(14)$$

Here, the derivatives are calculated at $A = A_*$. For Lennard-Jones potential $A_* \approx 1.0286a$. In Section 5.3 it is shown that in the vicinity of the point $A = A_*$ the thermal expansion of the chain is negative at small thermal energies and positive at high thermal energies.
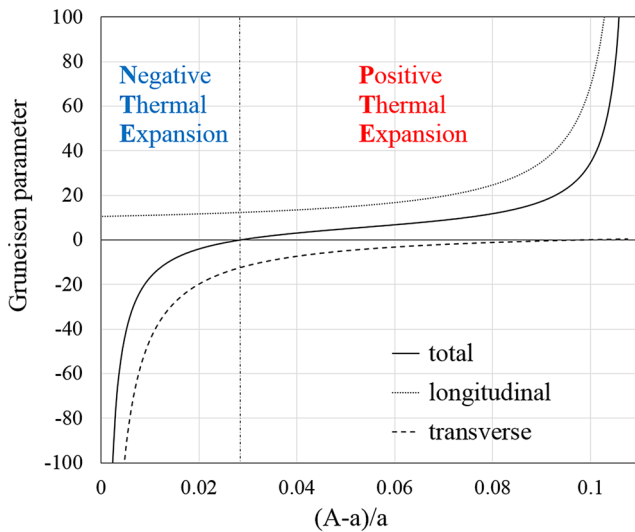
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Figure 1 Dependence of longitudinal, transverse, and total Grüneisen parameters on deformation of the Lennard-Jones chain calculated using formulas (11). Vertical line at $(A_* - a)/a$ separates regions of positive and negative thermal expansion. A_* is calculated using Eq. (14).

Thus at small thermal energies the chain demonstrate negative, zero or positive thermal expansion depending on deformation. There are two values of deformation corresponding to infinite Grüneisen parameter, and one deformation corresponding to zero Grüneisen parameter. In these cases quasi-harmonic approximation and corresponding Mie–Grüneisen equation of state are insufficient. Therefore in the following section more accurate equation of state accounting for anharmonic effects is derived.

4 Nonlinear, nonmonotonic thermal expansion at small deformations Consider thermal expansion at small deformations of the chain. In this case the transverse deformations of bonds are larger than the longitudinal, i.e., $\langle \alpha^2 \rangle \ll \langle \beta^2 \rangle$ (see formula (10)). The relation between these parameters is given by the equipartition theorem. Series expansion of Eq. (8) up to the forth order yields

$$\left(\Pi' + 2\Pi'' A^2 \right) \langle \alpha^2 \rangle = \Pi' \langle \beta^2 \rangle + \Pi'' A \langle \alpha\beta^2 \rangle + \Pi'' \langle \beta^4 \rangle. \tag{15}$$

Here $\langle \alpha^3 \rangle$, $\langle \alpha^2 \beta^2 \rangle$, $\langle \alpha^4 \rangle$ are neglected, because longitudinal deformations are smaller than transverse. Note that in the given approximation the correlation between longitudinal and transverse deformations $\langle \alpha\beta^2 \rangle$ is important. Similar series expansions are carried out for the thermal pressure p_T and the thermal energy E_T:

$$p_T = -2 \left(3\Pi'' + 2\Pi''' A^2 \right) A \langle \alpha^2 \rangle - 2\Pi'' A \langle \beta^2 \rangle$$
$$- 2 \left(\Pi'' + 2\Pi''' A^2 \right) \langle \alpha\beta^2 \rangle - \Pi''' A \langle \beta^4 \rangle,$$

$$E_T = 2 \left(\Pi' + 2\Pi'' A^2 \right) \langle \alpha^2 \rangle + 2\Pi' \langle \beta^2 \rangle$$
$$+ 5\Pi'' A \langle \alpha\beta^2 \rangle + \frac{3}{2} \Pi'' \langle \beta^4 \rangle. \tag{16}$$

Formula (16) implies that thermal pressure and thermal energy depend on parameters $\langle \alpha^2 \rangle, \langle \beta^2 \rangle, \langle \alpha\beta^2 \rangle, \langle \beta^4 \rangle$. The only relation between these parameters is given by the Eq. (15). Therefore, two additional equations are required in order to obtain the equation of state in a closed form. The following relations are used

$$\langle \beta^4 \rangle = \lambda \langle \beta^2 \rangle^2, \qquad A \langle \alpha\beta^2 \rangle = \mu \langle \beta^2 \rangle^2. \tag{17}$$

Parameter λ is estimated as follows. Assume that β is normally distributed quantity with dispersion $\langle \beta^2 \rangle$. Then $\langle \beta^4 \rangle$ is calculated as

$$\langle \beta^4 \rangle = \frac{1}{\sqrt{2\pi \langle \beta^2 \rangle}} \int_{-\infty}^{\infty} \beta^4 \exp \left(-\frac{\beta^2}{2 \langle \beta^2 \rangle} \right) = 3 \langle \beta^2 \rangle^2. \tag{18}$$

Therefore in the case of normal distribution $\lambda = 3$. In all simulations carried out in the present paper [1] $\lambda \in [2.89; 3]$, $\mu \in [-1; -0.92]$. Therefore the dependence of λ and μ on deformation of the chain and thermal energy is neglected.

Substituting the expressions (17) into the system (16) and excluding $\langle \beta^2 \rangle$ yields the equation of state in the explicit form:

$$p_T = \frac{B_2}{B_4} E_T + \frac{(B_2 B_3 - B_1 B_4)(B_3 - \sqrt{B_3^2 + 4B_4 E_T})}{2B_4^2}, \tag{19}$$

where

$$B_1 = -\frac{2}{A} \left(\Pi'' A^2 - \Gamma_l \Pi' \right), \quad B_3 = 4\Pi', \quad B_4 = \frac{7}{2}(\lambda + 2\mu)\Pi'',$$

$$B_2 = -\frac{2}{A}(\mu - \Gamma_l(\lambda + \mu))\Pi'' - (\lambda + 4\mu)\Pi''' A. \tag{20}$$

In contrast to Mie–Grüneisen equation of state, the dependence of pressure on thermal energy given by Eq. (19) is nonlinear. To show the significance of the nonlinearity, expand the Eq. (19) into series with respect to the thermal energy E_T. The expansions for the cases of (i) stretched chain ($A > a$), (ii) unstretched chain ($A = a$), and (iii) zero Grüneisen parameter $A = A_*$ are as follows:

$$p_T \approx \frac{\Gamma(A)}{A} E_T + \frac{B_2 A - \Gamma(A) B_4}{16\Pi'^2 A} E_T^2, \quad A > a, \tag{21}$$

$$p_T \approx -2 \left(\frac{2\Pi''(a) a^2}{7(\lambda + 2\mu)} \right)^{\frac{1}{2}} \sqrt{E_T}, \quad A = a, \tag{22}$$

$$p_T \approx \frac{B_2}{16\Pi'^2} E_T^2, \quad A = A_*. \tag{23}$$

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[1] Deformations up to 4% are considered. At higher deformations Mie–Grüneisen equation is sufficient (see Section 5.3)

Formulas (22) and (23) show that thermal expansion of the chain at $A = a$ and $A = A_*$ is strongly nonlinear. In these cases linear approximation of the dependence $p_T(E_T)$ given by Mie–Grüneisen equation is inaccurate. The Eq. (22) also answers the question why Grüneisen parameter of the unstretched chain is infinite. In this case the dependence $p_T(E_T)$ has *square root* asymptotic at small E_T. Therefore Grüneisen parameter characterizing the slope of this dependence at $E_T = 0$ is infinite. Note that the right-hand side of Eq. (22) does not depend on anharmonic properties of the potential Π. Therefore, the effect of strongly nonlinear thermal expansion of the unstretched chain is caused by geometrical nonlinearity of transverse vibrations rather than anharmonicity of the potential.

According to formula (21) the nonlinearity of the dependence $p_T(E_T)$ is also significant at small deformations, because the quadratic term in Eq. (21), proportional to $1/\Pi'^2$, is large. Moreover at some values of $A \in (a; A_*)$ the quadratic term leads to *nonmonotonic* thermal expansion, negative at small thermal energies and positive at large thermal energies (see Fig. 4).

5 Comparison with results of molecular dynamics simulations

5.1 Simulation details
In the present section the predictions of the nonlinear equation of state (19) are compared with the results of molecular dynamics simulations. Dynamics of the Lennard-Jones chain consisting of 10^3 particles in two space dimensions is simulated in NVE ensemble. Periodic boundary conditions in the direction of the chain are used. [2] Only interactions of the nearest neighbors are taken into account. Initially the particles are equally spaced and have random velocities uniformly distributed in a circle. Equations of motion of the particles are solved numerically using symplectic leap-frog integration scheme [24] with the time step $0.02T_*$, where T_* is a period corresponding to the Einstein frequency. During the simulation the pressure and thermal energy are calculated by the definitions (2) and (3), where averaging is carried out over 10^6 time steps. For each deformation and thermal energy 15 simulations with different initial conditions are performed.

5.2 Nonlinear thermal expansion at small deformations
Dependencies of thermal pressure on the thermal energy for the undeformed chain calculated using (i) molecular dynamics simulations and (ii) nonlinear equation of state (19) (for $\lambda = 2.99$, $\mu = -0.93$) are shown in Fig. 2. Here and below every point on the plot corresponds to the average over 15 molecular dynamics simulations with different initial conditions. The thermal energy and the thermal pressure are divided by ε_0 and ε_0/a, respectively. The maximum value of the thermal energy shown in Fig. 2 corresponds to breakage of the chain. Evidently the dependence of thermal pressure on thermal energy is strongly nonlinear and therefore cannot be described using Mie–Grüneisen
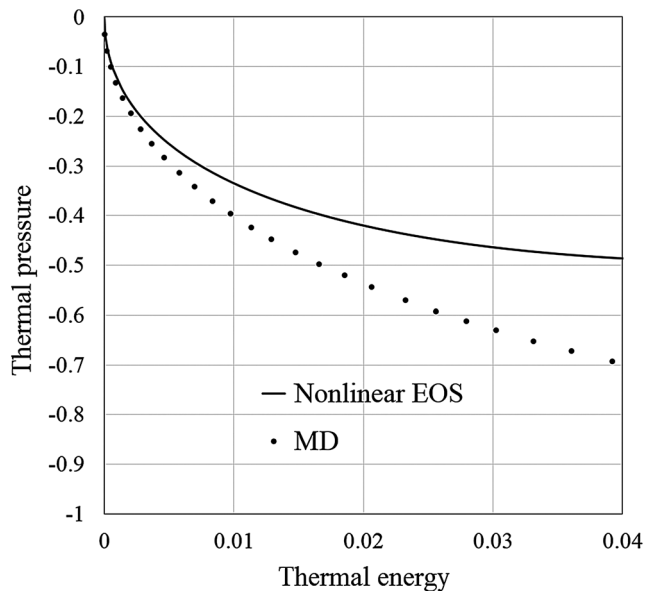

Figure 2 Dependence of thermal pressure on thermal energy for undeformed Lennard-Jones chain. The dispersion of the results of molecular dynamics simulations is of order of the size of the points.

equation of state (11). In contrast, the nonlinear equation of state (19) correctly predicts *square root asymptotic* of the dependence $p_T(E_T)$ at small thermal energies.

The dependence of the thermal pressure on the thermal energy for the chain stretched by 0.1% and 1% is shown in Fig. 3. Mie–Grüneisen equation of state (11) gives correct slope of the dependence $p_T(E_T)$ at $E_T = 0$. However at finite thermal energies it is inaccurate, since the quadratic term in the expansion (21) is large. For example, maximum error of Mie–Grüneisen equation for $A = 1.01a$ is more than 200%. For $A = 1.001a$ the error is even larger. At the same time the nonlinear equation of state (19) reproduces the results of molecular dynamics simulations in the entire range of thermal energies. Maximum error at high thermal energies is about 30%.

5.3 Nonmonotonic thermal expansion. Large deformations
Formula (14) implies that Grüneisen parameter of the Lennard-Jones chain is equal to zero for $A_* \approx 1.0286a$. Consider the behavior of the chain in the vicinity of this point in more details. Dependencies of thermal pressure on thermal energy for $A = 1.028a$ and $A = 1.0286a$ are shown in Fig. 4. For $A = 1.0286a$ the thermal expansion is zero at $E_T \to 0$ and positive for higher thermal energies. Asymptotic behavior at small thermal energies is described by Eq. (23), i.e., thermal pressure is proportional to the *square* of the thermal energy. Therefore thermal expansion coefficient tends to zero as thermal energy tends to zero. Note that similar phenomenon is usually observed in quantum systems.

For $A = 1.028a$ the dependence $p_T(E_T)$ is nonmonotonic. Therefore thermal expansion of the chain is *negative at low thermal energies and positive at high thermal energies*. In contrast to Mie–Grüneisen equation of state (11), the

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[2]Periodic boundary conditions allow to avoid the finite size effects.

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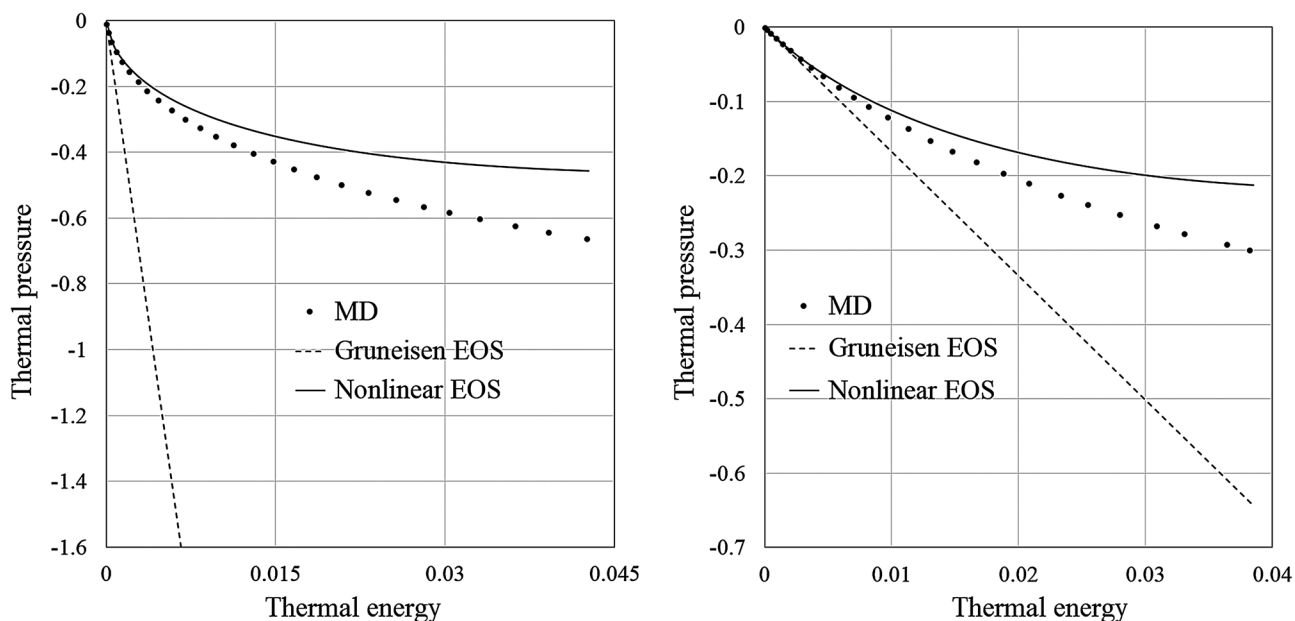Phys. Status Solidi B 252, No. 7 (2015)   1669

Figure 3 Dependence of thermal pressure on thermal energy for Lennard-Jones chain stretched by 0.1% (left) and 1% (right). The dispersion of the results of molecular dynamics simulations is of order of the size of the points.

nonlinear equation of state (19) qualitatively describes this phenomenon. Quantitative discrepancy is cased by the fact that Eq. (19) is derived for the case of small deformations.

Further increase of the deformation leads to decrease of the maximum thermal energy corresponding to breakage of the chain. In this case the dependence of the thermal pressure on thermal energy is almost linear (see Fig. 5). Therefore, at large deformations the behavior of the chain can be accurately described by Mie–Grüneisen equation of state.

Finally let us note that at all deformations the second co-efficient in the expansion (21) of $p_T(E_T)$ with respect to E_T is positive. Therefore Mie–Grüneisen equation of state under-estimates the pressure (see Figs. 3, 4, and 5). Three dimen-sional crystals with pair interactions demonstrate opposite behavior [20]. In three dimensions Mie–Grüneisen equation overestimates the pressure. At the same time the nonlinearity of the dependence $p_T(E_T)$ in three dimensions is significantly weaker [20].
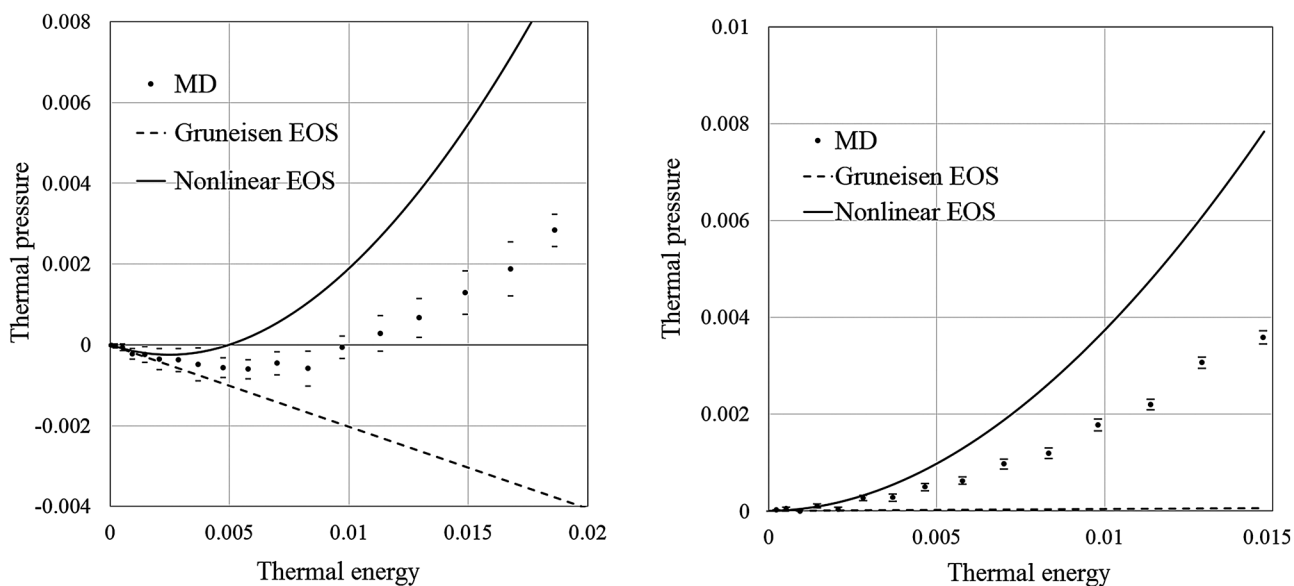

Figure 4 Dependence of thermal pressure on thermal energy for Lennard-Jones chain stretched by 2.8% (left) and 2.86% (right). The bars show standard error of the results of molecular dynamics simulations.
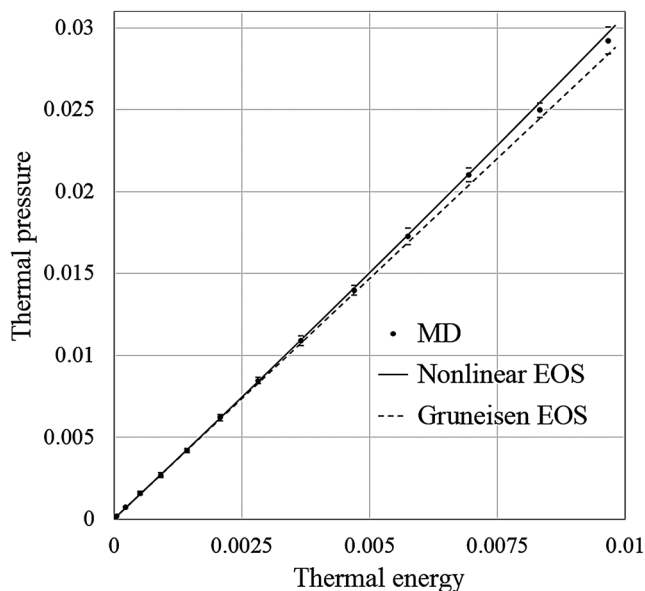
Figure 5 Dependence of thermal pressure on thermal energy for Lennard-Jones chain stretched by 4%. The bars show the dispersion of the results of molecular dynamics simulations.

6 Conclusions Thermal expansion of a chain with longitudinal and transverse vibrations was investigated analytically and numerically. Corresponding equations of state were derived using series expansion of pressure and thermal energy with respect to deformations of the bonds caused by thermal motion. The slope of the dependence of thermal pressure on the thermal energy at zero thermal energy is described by Grüneisen parameter. For Lennard-Jones-like potential Grüneisen parameter smoothly changes from $-\infty$ to $+\infty$ as deformation of the chain changes from 0 to the critical value. It was demonstrated analytically and numerically that the dependence of thermal pressure on the thermal energy is strongly nonlinear at small deformations of the chain. In particular, at some deformations the dependence is non-monotonic. In this case quasi-harmonic approximation and linear Mie–Grüneisen equation of state are inapplicable.

The nonlinear equation of state (19) was derived. In contrast to Mie–Grüneisen equation, the nonlinear equation of state qualitatively describes the behavior of the chain at all deformations and thermal energies. In particular, the equation implies that the dependence of thermal pressure on thermal energy for the unstretched chain has *square root* asymptotic at small thermal energies.

At deformation corresponding to zero Grüneisen parameter the thermal pressure is proportional to square of thermal energy. Therefore thermal expansion coefficient tends to zero at low temperatures. Similar behavior is usually observed in *quantum* systems. Classical systems usually have non-zero thermal expansion coefficient at zero temperature.

The nonlinear equation of state also predicts that at some deformations the thermal expansion of the chain is nonmonotonic, i.e., it is negative at low thermal energies and positive at high thermal energies. Similar phenomenon was observed

in computer simulations of graphene [23] and hybrid materials [16].

Additionally, the analysis presented in the paper suggests that the thermal expansion is strongly nonlinear in the vicinity of *instability*.[3] Therefore strongly nonlinear thermal expansion is expected in nanowires and graphene under compression close to buckling. This theoretical prediction is awaiting confirmation by computer simulations and real experiments.

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[3]For example, unstretched chain is unstable under compression.