

Analysis of Equations of State and Determination of the Grüneisen Function for Two-Dimensional Crystal Lattices[#]

A. Yu. Panchenko^{a,b*}, E. A. Podolskaya^{a,b}, and A. M. Krivtsov^{a,b}

Presented by Academician N.F. Morozov May 23, 2016

Received June 10, 2016

Abstract—The method of particle dynamics is used for both analytical and numerical investigation of tensor properties of the Mie–Grüneisen equation of state for two-dimensional solids with crystalline structure. It is demonstrated analytically that the Grüneisen function essentially depends on the ratio between the eigenvalues of the deformation temperature tensor, which, in this work, is determined numerically.

DOI: 10.1134/S1028335817030077

Advances in nanotechnology have led to the necessity of determining mechanical properties of solids with a microstructure in a wide range of temperatures and stress-strain states [1]. For this purpose, the Mie–Grüneisen equation of state can be used in the case of high pressures and temperatures. Herein, the material parameter, i.e., the Grüneisen coefficient that represents the relationship between pressure, volume, and internal energy, is scalar [2]. Generally, the scalar Grüneisen coefficient may not account for the tensor nature of the thermal stresses in crystals. The latter becomes possible if one introduces (i) the tensor Grüneisen function [3, 4] or (ii) the tensor temperature [5, 6]. The equations of state for crystalline solids regarding the first concept are considered in [3], and the second one is taken into account in [7]. The aim of the present paper is to obtain an asymptotically exact equation of state taking both ideas into consideration.

DERIVATION OF THE EQUATION OF STATE

The generalization of the classical Mie–Grüneisen equation for ideal crystals of any dimension is derived in [3]:

$$\tilde{\boldsymbol{\tau}} = -\frac{1}{V}\boldsymbol{\Gamma}\tilde{U}_T, \quad (1)$$

[#] The article was translated by the authors.

^a Peter the Great St. Petersburg Polytechnic University, St. Petersburg, 195251 Russia

^b Institute for Problems in Mechanical Engineering, Russian Academy of Sciences, St. Petersburg, Russia

*e-mail: artemqt@yandex.ru

where V is the unit cell's volume, $\tilde{\boldsymbol{\tau}}$ is the stress tensor, induced by thermal motion, $\boldsymbol{\Gamma}$ is the Grüneisen function, which is also a tensor, and \tilde{U}_T is the internal energy of the system, calculated as the sum of the kinetic \tilde{K} and potential \tilde{U} energies:

$$\begin{aligned} \tilde{U}_T &= \tilde{K} + \tilde{U}, & \tilde{K} &= \frac{m}{2} \sum_k \dot{u}_k^2, \\ \tilde{U} &= \frac{1}{2} \sum_k (\langle \Pi(A_k) \rangle - \Pi(\hat{A}_k)). \end{aligned} \quad (2)$$

Here the motion of the particles is divided into “fast” (oscillatory) and “slow” (“cold”) parts [8] and the corresponding values are denoted by \sim and \wedge ; m is the particle mass, \dot{u}_k is the length of the velocity vector (calculated with respect to the system's center of mass), and Π is the interaction potential. Operator $\langle \cdot \rangle$ denotes averaging, first, over space, then, by time, and afterwards, over the ensemble; vector $A_k = |A_k|$, $A_k = \hat{A}_k + \tilde{A}_k$ connects the reference particle and the particle with the number k , and $\hat{A}_k = \langle A_k \rangle$. The zero point of the potential energy corresponds to the stationary state, and the total momentum of the system remains zero as the temperature increases.

The expression for the Cauchy stress tensor (3) in a discrete system in the presence of thermal motion is derived in [3]:

$$\boldsymbol{\tau} = \frac{1}{2V} \sum_k \langle A_k \rangle \langle \mathbf{F}_k(\mathbf{r}) \rangle, \quad (3)$$

where \mathbf{F}_k is the force acting on the reference particle.

For pair force interaction $\mathbf{F}_k = \frac{\Pi'_k}{A_k} \mathbf{A}_k$, where

$\Pi'_k = \Pi'(A_k)$, and there is no summation over repeated indices. If a lattice is stress-free before heating, then $\boldsymbol{\tau} = \tilde{\boldsymbol{\tau}}$. Derivation of the equation of state [3] is based on the Taylor expansion of expressions (2) and (3) in the vector $\tilde{\mathbf{A}}_k$ and their subsequent averaging. We restrict ourselves to the first nonzero term in the expansion after averaging. Hence, the equations for the thermal parts of the stress tensor and the internal energy can be written in the following form:

$$\tilde{\boldsymbol{\tau}} = \frac{1}{4V} \sum_k [\alpha_k (\hat{\mathbf{A}}_k \hat{\mathbf{A}}_k \mathbf{E} + 2\hat{\mathbf{A}}_k \mathbf{E} \hat{\mathbf{A}}_k) + \beta_k \hat{\mathbf{A}}_k \hat{\mathbf{A}}_k \hat{\mathbf{A}}_k \hat{\mathbf{A}}_k] \cdot \langle \tilde{\mathbf{A}}_k \tilde{\mathbf{A}}_k \rangle, \quad (4)$$

$$\tilde{U}_T = \frac{1}{2} \sum_k [\alpha_k \hat{\mathbf{A}}_k \hat{\mathbf{A}}_k + \gamma_k \mathbf{E}] \cdot \langle \tilde{\mathbf{A}}_k \tilde{\mathbf{A}}_k \rangle, \quad (5)$$

where

$$\alpha_k = \frac{\hat{\Pi}_k'' \hat{A}_k - \hat{\Pi}_k'}{\hat{A}_k^3}, \quad \beta_k = \frac{\hat{\Pi}_k''' \hat{A}_k^2 - 3\hat{\Pi}_k'' \hat{A}_k + 3\hat{\Pi}_k'}{\hat{A}_k^5},$$

$$\gamma_k = \frac{\hat{\Pi}_k'}{\hat{A}_k}.$$

Thus, for a simple crystal lattice in thermodynamic equilibrium, the only unknown variable is tensor $\langle \tilde{\mathbf{A}}_k \tilde{\mathbf{A}}_k \rangle$, which will be further referred to as the deformation temperature tensor.

THE DEFORMATION TEMPERATURE AND THE GRÜNEISEN FUNCTION

Let us introduce the unit vectors of the 2-D Cartesian coordinate system for each bond: \mathbf{e}_x is directed along the bond, \mathbf{e}_y is orthogonal to it; let us also restrict ourselves to the interaction of nearest neighbors. Then, the components of the deformation temperature tensor will have a simple physical meaning, i.e., the square of thermal deformation of the bond along its initial direction is equal to $\langle \tilde{\mathbf{A}}_k \tilde{\mathbf{A}}_k \rangle_{xx} / a^2$ and that in the orthogonal direction is $\langle \tilde{\mathbf{A}}_k \tilde{\mathbf{A}}_k \rangle_{yy} / a^2$. It is obvious that due to the symmetry of the tensor $\langle \tilde{\mathbf{A}}_k \tilde{\mathbf{A}}_k \rangle$, its components in these axes are the same for all bonds. Let

$$\Theta = \frac{\langle \tilde{\mathbf{A}}_k \tilde{\mathbf{A}}_k \rangle_{yy}}{\langle \tilde{\mathbf{A}}_k \tilde{\mathbf{A}}_k \rangle_{xx}}. \quad (6)$$

The generalized expression of the scalar Grüneisen coefficient, which contains a variable $f = \Theta + 1$, can be written for the three-dimensional problem [2]. If the tensor function [3] is used, the trace of which corresponds to the Zubarev–Vashchenko formula [2, 9], the values of the internal energy and the stress tensor components are 20 and 24% larger than those

obtained in the present work as a result of the numerical simulation, respectively. However, as the corrections to these values have the same sign, the error in the Grüneisen coefficient totals only 3%. In [7] the coefficient f was determined using molecular dynamics simulation for several values of temperature at hydrostatic compression of the FCC lattice. Further, f was considered only as a fitting parameter without taking into account its physical sense [10]; investigation of the influence of deformation and temperature on f is carried out for the problems of the Earth's core and mantle (at high pressure) [11].

In the present work, the method of particle dynamics [12] is used to determine the coefficient Θ . We study a square sample with a triangular lattice (11500 particles), and periodic boundary conditions¹ are used. The interaction between the particles is described by the Morse potential:

$$\Pi(A_k) = D[e^{2\alpha(1-A_k/a)} - 2e^{\alpha(1-A_k/a)}], \quad (7)$$

where D is the depth of the potential well, a is the equilibrium bond distance, and α is responsible for the well width. Initially, the particles are placed in lattice nodes, random velocities are set so that the average kinetic energy per particle is equal to $2 \times 10^{-5} D$, and the system's center of mass remains fixed. Then, the equations of motion are integrated using the Verlet algorithm and the calculation step is $T_0/100$, where T_0 is the period of small oscillations of an isolated pair of particles. The cutoff radius is located between the first and second coordination spheres, and it is equal to $1.36a$.

Simulation results after averaging over space and over 250 realizations with the same initial energy level demonstrate that the components of the deformation temperature tensor converge to the equilibrium value quite rapidly (within a few periods T_0) with a standard deviation of 1.1%. The off-diagonal components are approximately three orders of magnitude smaller than the diagonal ones; hence, \mathbf{e}_x and \mathbf{e}_y can be regarded as eigenvectors of the deformation temperature tensor. The high-frequency nature of the principal mode allows us to limit the averaging time by several dozen T_0 . Substituting tensor $\langle \tilde{\mathbf{A}}_k \tilde{\mathbf{A}}_k \rangle$ in diagonal form into (4) and (5) and, again, taking into account only the nearest neighbor interaction (in this case \hat{A}_k and $\hat{\Pi}_k$ do not depend on k), we obtain

$$\boldsymbol{\Gamma} = -\frac{1}{2N\hat{A}^2} \frac{\hat{A}^2 \hat{\Pi}'''' + \Theta \hat{A} \hat{\Pi}''' - \Theta \hat{\Pi}'}{\hat{A} \hat{\Pi}'' + \Theta \hat{\Pi}'} \sum_k \hat{\mathbf{A}}_k \hat{\mathbf{A}}_k, \quad (8)$$

where N is the number of particles that belong to the first coordination sphere.

¹ The sample's volume and shape are fixed, which blocks thermal expansion and causes thermal stresses.

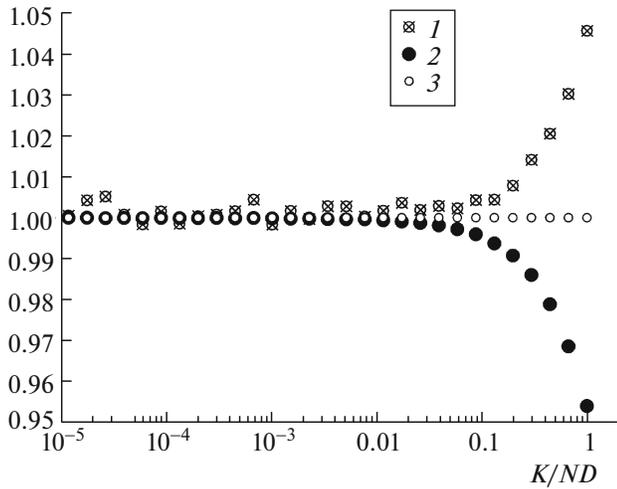


Fig. 1. Dependence of the ratios between (1) diagonal components of the deformation temperature Θ (in terms of Θ_0), (2) spherical parts of the Grüneisen functions Γ_e (1)–(3) and Γ (8), (3) diagonal components of the Grüneisen function Γ_e on the initial average kinetic energy per particle (in terms of D). Here and in Figs. 2 and 3:

$$(1) \frac{\Theta}{\Theta_0}, (2) \frac{\Gamma_e}{\Gamma}, (3) \frac{\Gamma_{e,yy}}{\Gamma_{e,xx}}.$$

Hereinafter, let us denote the Grüneisen function, calculated by formula (1) using the values of the internal energy (2) and the stress tensor (3) obtained during the numerical simulation, as Γ_e .

INFLUENCE OF THE THERMAL MOTION RATE AND STRAIN ON THE GRÜNEISEN FUNCTION

As a result of simulation for a stress-free triangular lattice, the ratio between the diagonal components of the deformation temperature tensor $\Theta = \Theta_0 = 1.435 \pm 0.016$ is obtained. It is also shown that neither the size of the system, nor the type of the pair central potential (the Morse potential, the harmonic potential, and the Lennard-Jones potential were considered), nor the account for the interaction with the next coordination spheres has any influence on the value of Θ . An increase of ten times in the thermal motion rate leads to an increase in Θ by 4.5% (see Fig. 1). It is demonstrated that the deviation of the spherical part Γ of the Grüneisen function (8) from Γ_e , obtained as a result of the numerical simulation, also does not exceed 4.5%; consideration of the next members in the expansion of the deformation temperature is required to reduce this error.

It has been discovered that a significant change in the ratio between the diagonal components of the deformation temperature and the Grüneisen function is only possible at a finite uniform strain. The depen-

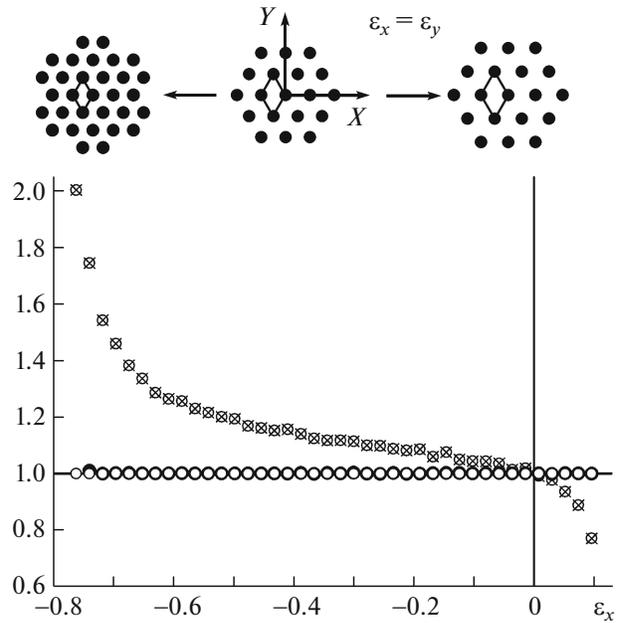


Fig. 2. Dependence of the ratios between (1) diagonal components of the deformation temperature Θ (in terms of Θ_0), (2) spherical parts of the Grüneisen functions Γ_e (1)–(3) and Γ (8), and (3) diagonal components of the Grüneisen function Γ_e on volumetric strain. The strain tensor eigenvectors, lattice structure with respect to the stress-free configuration (in the center), the unit cell, and the relation between the components of the strain tensor are shown above the graph.

dence of these values on ϵ_x for the volumetric strain and distortion are shown in Figs. 2 and 3; ϵ_x and ϵ_y are the linear parts of the right Cauchy–Green strain tensor; the axes x and y correspond to the direction along the bond of the reference particle with its the nearest neighbor and the orthogonal direction. Tension along the hydrostatic line (Fig. 2) leads to a decrease in coefficient Θ , and the loss of stability happens due to the strain in the longitudinal bonds; i.e., some bonds get broken. At 80% volumetric compression, the value of Θ doubles. This means that the deformation in the direction orthogonal to the bonds is significantly higher than the longitudinal deformation, i.e., shear buckling takes place.

At the same time, due to the lattice symmetry, the Grüneisen function is a spherical tensor.

When approaching the boundaries of the stability region in the strain space² along the constant volume lines (Fig. 3), Θ tends to infinity, which also indicates the shearing mechanism of the stability loss. Furthermore, the ratio between the diagonal components of the Grüneisen function essentially depends not only

² See [13, 14] on determination of the triangular lattice stability regions in the strain space and the physical sense of their boundaries.

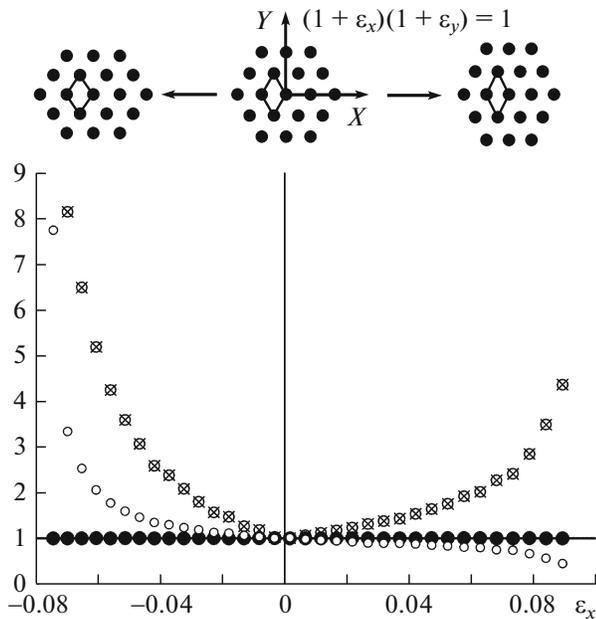


Fig. 3. Dependence of the ratios between (1) diagonal components of the deformation temperature Θ (in terms of Θ_0), (2) spherical parts of the Grüneisen functions Γ_e (1)–(3) and Γ (8), (3) diagonal components of the Grüneisen function Γ_e on distortion. The strain tensor eigenvectors, lattice structure with respect to the stress-free configuration (in the center), the unit cell, and the relation between the components of the strain tensor are shown above the graph.

on the strain tensor deviator but also on the stability boundary considered. This fact demonstrates the need for use of the Mie–Grüneisen equation of state in tensor form.

CONCLUSIONS

To sum up, in the present work, the Mie–Grüneisen equation of state for a simple two-dimensional lattice is obtained in tensor form, being asymptotically exact at a low level of thermal motion. It is shown that the scalar Grüneisen coefficient does not allow us to describe the lattice state in the presence of shear deformation; i.e., the tensor nature of the Grüneisen function has to be accounted for. At the same time, the ratio between the components of the deformation temperature tensor has a strong influence on the value of the Grüneisen function for any strain.

The developed constitutive equation can be used in software for modeling of thermomechanical processes in solids. The results of this work allowed us to increase the accuracy of calculation of the stress state by 20%.

ACKNOWLEDGMENTS

The authors are grateful to V.A. Kuzkin, N.F. Morozov, and A.B. Freidin for helpful discussions and valuable comments.

This work was supported by the Ministry of Education and Science of the Russian Federation within the project part of the state task in the field of scientific activity (no. 9.2091.2014/K) and by the President of the Russian Federation (grant no. MK-1820.2017.1).

REFERENCES

1. R. V. Goldstein and N. F. Morozov, *Phys. Mesomechan.* **10** (5–6), 235 (2007).
2. O. L. Anderson, *Geophys. J. Int.* **143**, 279 (2000).
3. A. M. Krivtsov and V. A. Kuzkin, *Mech. Solids* **46** (3), 387 (2011).
4. V. A. Kuzkin and A. M. Krivtsov, *Phys. Status Solidi B* **252** (7), 1664 (2015).
5. B. L. Holian, W. G. Hoover, B. Moran, and G. K. Straub, *Phys. Rev. A* **22** (6), 2798 (1980).
6. W. G. Hoover and C. G. Hoover, *Phys. Rev. E* **81**, 046302 (2010).
7. M. A. Barton and F. D. Stacey, *Phys. Earth Planet. In.* **39**, 167 (1985).
8. I. I. Blehman, *Theory of Vibration Processes and Devices. Vibrational Mechanics and Vibrational Rheology* (Ruda i Metalli, St. Petersburg, 2013), p. 640 [in Russian].
9. V. Ya. Vashchenko and V. N. Zubarev, *Sov. Phys. Solid State* **5**, 653 (1963).
10. C. Nie, B. Zong, and J. Wang, *Physica B: Condens. Matter* **468–469**, 7 (2015).
11. F. D. Stacey and P. M. Davis, *Phys. Earth Planet. In.* **142**, 137 (2004).
12. A. M. Krivtsov, *Deformation and Fracture of Solids with Microstructure* (Fizmatlit, Moscow, 2007), p. 304 [in Russian].
13. E. A. Podolskaya, A. Yu. Panchenko, A. M. Krivtsov, and P. V. Tkachev, *Dokl. Phys.* **57** (2), 92 (2012).
14. E. A. Podolskaya, A. Yu. Panchenko, A. B. Freidin, and A. M. Krivtsov, *Acta Mech.* **227** (1), 185 (2016).