

# Comparison of approaches based on statistical physics and particle dynamics for equations of state derivation

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## Abstract

Behavior of a particle in a potential well is considered. Methods of statistical physics are used. Method for statistical sum calculation is proposed. Expression for the statistical sum in the form of power series is derived. Mie-Gruneisen and more precise equations of state are derived. Comparison of the obtained results with the exact and approximate solutions obtained by the particle dynamics method is conducted.

## 1 Introduction

The problem of equation of state (EOS) obtaining is still a serious challenge for the modern physics of condensed matter. Laws of thermodynamics and general principles can give only main limitation for EOS [1, 2]. Thus one has to use various empirical equations, which can lead to certain instabilities and physically incorrect results [3].

An attractive way of solving this problem is to develop simple mechanical models which allow analytical obtaining of the desired equations. The simplest model of this kind is a particle in the potential well, which can be considered as approximation of the dynamics of an atom of crystal. One of the classical ways of the EOS obtaining is to analyze the statistical sum of the system [4]. In case of harmonic potential of the interatomic interactions this approach allows to the desired EOS in Mie-Gruneisen form which declare the following linear relation between pressure and thermal energy

$$p = p(V, E_T) = p_0(V) + \Gamma(V) \frac{E_T}{V}, \quad (1)$$

where  $\Gamma(V)$  is so-called Gruneisen function of volume  $V$ . The anharmonic correction to the Gruneisen function was considered in [5].

Another way was proposed in works [6, 7, 8], where EOS obtaining was based on particle dynamics method [8, 9, 10, 11]. According to this method the medium is represented by a great number of interacting particles. The particles are moving in accordance with the laws of classical dynamics of Newton. Further microscopic analogues of pressure, thermal energy and other macroscopic values are introduced. Time averaging and expansion into a series in terms of small thermal parameter are carried out. Thus for models considered in works [6, 7, 8] Mie–Gruneisen equation was derived and the dependence of Gruneisen function on volume was obtained. In particular it was shown that Mie–Gruneisen EOS does not work for large tensile deformations. The more accurate EOS was derived. The exact EOS for the particle in the potential well was obtained in [12].

This paper is devoted to the comparison of the approaches mentioned above. The new method of statistical sum calculation is proposed. The influence of anharmonic terms in the potential of interatomic interactions is investigated. The generalization of Mie–Gruneisen EOS, essential for large tensile deformations and thermal energy, is obtained.

## 2 Main designations

Let us represent the material as a large number of independent anharmonic oscillators. Interactions between different oscillators can be approximately taken into account if we assume that the oscillator behaves like a particle in the potential well with random value of energy. Let us also assume that particle interacts with walls of the well by means of potential  $\Pi$ . Then the hamiltonian of the system has the following form

$$H = \frac{p^2}{2m} + U(x), \quad U(x) = \Pi(b + x) + \Pi(b - x), \quad (2)$$

where  $p$  is momentum of the particle,  $x$  is its coordinate ( $x = 0$  corresponds to the middle of the well),  $b$  is half of the distance between walls. Let us denote the specific volume as  $V = 2b$  and the potential energy as a sum of “cold” component  $U_0(V)$  and thermal component  $U_T(V, T)$ . “Cold” component corresponds to the deformation of the potential well. It is function of volume only. Thermal component depends on both volume and temperature.

$$U_T \stackrel{\text{def}}{=} U - U_0, \quad U_0 = 2\Pi(b) \quad (3)$$

Following the book [4], let us introduce the statistical sum  $Z$

$$Z = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta H(p,x)} dp dx, \quad \beta = 1/kT \quad (4)$$

where  $\hbar$  is Plank constant,  $k$  is Boltzman constant,  $T$  is temperature. Integrating equation (4) with respect to  $p$ , one can obtain

$$Z = \frac{Z_0}{\sqrt{\beta}} e^{-\beta U_0} \int_{-\infty}^{\infty} e^{-\beta U_T} dx. \quad (5)$$

where  $Z_0 = \sqrt{\frac{m}{2\pi\hbar^2}}$ . According to the definition [4] Helmholtz free energy can be calculated by the following formula.

$$F \stackrel{\text{def}}{=} -\frac{1}{\beta} \ln Z = U_0 - \frac{1}{\beta} \ln \frac{Z_0}{\sqrt{\beta}} - \frac{1}{\beta} \ln \int_{-\infty}^{\infty} e^{-\beta U_T} dx \quad (6)$$

The classical definitions of pressure and internal energy are as follows [4]

$$p = -\left(\frac{\partial F}{\partial V}\right)_T, \quad E = \left(\frac{\partial \beta F}{\partial \beta}\right)_V. \quad (7)$$

Following [5], let us divide pressure and internal energy into “cold” and thermal components. Using formulae (6) and (7), one can obtain

$$p_0 \stackrel{\text{def}}{=} p|_{T=0} = -\frac{\partial U_0}{\partial V}, \quad p_T \stackrel{\text{def}}{=} p - p_0 = -\frac{\int_{-\infty}^{\infty} \frac{\partial U_T}{\partial V} e^{-\beta U_T} dx}{\int_{-\infty}^{\infty} e^{-\beta U_T} dx}, \quad (8)$$

$$E_0 \stackrel{\text{def}}{=} E|_{T=0} = U_0, \quad E_T \stackrel{\text{def}}{=} E - E_0 = \frac{1}{2}kT + \frac{\int_{-\infty}^{\infty} U_T e^{-\beta U_T} dx}{\int_{-\infty}^{\infty} e^{-\beta U_T} dx}.$$

Thus equations (8) represent the EOS in an implicit form. They can be rewritten in more compact form using the following averaging operator  $\langle f(x) \rangle \stackrel{\text{def}}{=} \int_{-\infty}^{\infty} f(x)n(x)dx$

$$p_T = -\frac{1}{2} \langle \Pi'(b+x) + \Pi'(b-x) \rangle, \quad (9)$$

$$E_T = \frac{1}{2}kT + \langle \Pi(b+x) + \Pi(b-x) \rangle - 2\Pi(b).$$

where  $n(x)$  is distribution function with respect to coordinates [13]

$$n(x) \stackrel{\text{def}}{=} \frac{e^{-\beta u}}{\int_{-\infty}^{\infty} e^{-\beta u} dx}. \quad (10)$$

In paper [7] the analogous expressions were obtained using time averaging of the equations of motion.

Cold characteristics are usually well known in contrast to the thermal one. The wide spread way of calculating the thermal characteristics is to use so-called quasiharmonic approximation [5]. Within the scope of this approximation  $\Pi = \frac{1}{2}C(b - a + x)^2$ ,  $C$  is function of volume,  $a$  is equilibrium distance. Then thermal component of potential energy has the following form

$$U_T = C(V)x^2, \quad (11)$$

where  $V = 2b$ ,  $V_0 = 2a$ . In this case the integral in formula (8) can be calculated. Then one can obtain the expression for the thermal pressure in Mie–Gruneisen form

$$p_T = \frac{\Gamma(V)}{V} E_T, \quad \Gamma(V) = -\frac{VC'(V)}{2C(V)}, \quad E_T = kT. \quad (12)$$

The expression for Gruneisen function is equal to the result of the paper [6]. Thus one can assume that for the case of linear oscillations (small thermal energies) time and coordinate averaging are equivalent.

### 3 Equation of state in the form of series

In order to estimate the influence of anharmonical terms on the EOS let us divide the potential energy into harmonic and anharmonical parts.

$$U_T = Cx^2 + U_{ah}, \quad U_{ah} \stackrel{\text{def}}{=} U_T - Cx^2. \quad (13)$$

Substituting formula (13) in formula (5) and expanding  $e^{-\beta U_{ah}(x)}$  in power series in terms of  $x$  one can obtain

$$Z = \frac{Z_0 e^{-\beta U_0}}{\sqrt{\beta}} \int_{-\infty}^{\infty} \sum_{i=0}^{\infty} e^{-\beta Cx^2} U_i(V, \beta) x^{2i} dx, \quad U_i(V, \beta) \stackrel{\text{def}}{=} \frac{1}{(2i)!} \left. \frac{d^{2i}(e^{-\beta U_{ah}})}{dx^{2i}} \right|_{x=0}. \quad (14)$$

Note that only such kind of expansion can give one opportunity to obtain the expression for statistical sum. For example, the direct expansion of  $e^{-\beta U_T}$  in formula (5) into power series leads to divergent integrals.

Let us interchange the integration and summation in formula (14). Also let us take into account the following identity

$$\int_{-\infty}^{\infty} e^{-\beta Cx^2} x^{2i} dx = \frac{\gamma(i + 1/2)}{\sqrt{C\beta} (C\beta)^i}, \quad (15)$$

where  $\gamma$  is Euler gamma function. Then substituting (15) in (14) one can obtain

$$Z = \frac{Z_0 e^{-\beta U_0}}{\sqrt{C\beta}} \sum_{i=0}^{\infty} U_i(V, \beta) \frac{\gamma(i + 1/2)}{(C\beta)^i}. \quad (16)$$

Using formula (16) one can calculate the exact formulae for pressure and internal energy. However, only finite number of terms are usually the matter of interest from the practical point of view. In appendix A it is shown that  $U_i(V, \beta)$  are polynoms of the  $[i/2]$  degree in terms of  $\beta$ . Therefore term number  $i$  in the sum (16) has the following order

$$U_i(V, \beta) \frac{\gamma(i + 1/2)}{(C\beta)^i} \sim \beta^{[i/2]-i} \quad (17)$$

Equation (17) gives one an opportunity to estimate the terms which are neglected.

Let us leave only terms of order till  $T^2$  in expression (16).

$$Z \simeq \frac{Z_0 \sqrt{\pi} e^{-\beta U_0}}{\sqrt{C}} kT \left( 1 - \frac{1}{32} \frac{U_{ah}^{(4)}}{C^2} kT \right), \quad (18)$$

It is obvious that first anharmonical term is essential in case of large temperatures. Let us calculate the thermal pressure and thermal energy accurate within  $T^2$ . Using formulae (2), (13) one can represent  $p_T$  and  $E_T$  in terms of interatomic potential  $\Pi$

$$\begin{cases} p_T = -\frac{\Pi'''}{4\Pi''} kT - \frac{\Pi^{(5)}\Pi'' - \Pi^{(4)}\Pi'''}{64\Pi''^3} (kT)^2 \\ E_T = kT - \frac{1}{32} \frac{\Pi^{(4)}}{\Pi''^2} (kT)^2. \end{cases} \quad (19)$$

Excluding the temperature from the system (19) one can obtain the desired EOS in the explicit form

$$p_T = -\frac{\Pi'''}{4\Pi''}E_T + \frac{\frac{3}{2}\Pi^{(4)}\Pi''' - \Pi^{(5)}\Pi''}{64\Pi''^3}E_T^2. \quad (20)$$

Let us compare EOS (20) with the result of paper [6]. The following EOS was obtained in paper [6] using particle dynamics method

$$p_T = f_2 \frac{\sqrt{f_1^2 + \frac{3}{2}\lambda f_3 E_T} - f_1}{\frac{3}{2}\lambda f_3}, \quad f_k = \frac{(-1)^{k+1}\Pi^{(k+1)}}{k!}, \quad \lambda = \frac{\langle x^4 \rangle}{\langle x^2 \rangle^2}, \quad (21)$$

where  $\langle \rangle$  denotes time averaging. Computer simulations have shown that  $\lambda \simeq 1.6$  and depend on temperature and volume weakly. Expanding equation (21) in a series in terms of  $E_T$  one can obtain

$$p_T = -\frac{\Pi'''}{4\Pi''}E_T + \frac{\lambda\Pi^{(4)}\Pi'''}{64\Pi''^3}E_T^2. \quad (22)$$

One can see that the second terms in equations (20) and (22) are different. However the derivation of formula (22) was based on the assumption that  $\lambda$  does not depend on thermal energy. Computer simulation shows that this dependence can be neglected only for relatively small thermal energies. Thus one can use formulae (22) and (20) in order to determine  $\lambda$ .

## 4 Critical deformation of the potential well

In paper [6] it was shown that EOS for the particle in the potential well strongly depends on the deformation of the well. Let us consider the deformation of the potential well, which corresponds to the maximum of the cold pressure. This case corresponds to the simplest model of the behavior of an atom in the elementary cell in the vicinity of failure. The critical distance between walls can be obtained from the following equation

$$C(\mathbf{b}_{cr}) \stackrel{\text{def}}{=} \Pi''(\mathbf{b}_{cr}) = 0 \quad (23)$$

By the analogy of the previous section let us divide the potential energy into two parts.

$$U_T = C_1 x^4 + \tilde{U}_T(x), \quad \tilde{U}_T \stackrel{\text{def}}{=} U_T - C_1 x^4. \quad (24)$$

Then one can obtain the following expression for statistical sum

$$Z = \frac{Z_0 e^{-\beta U_0}}{2 C_1^{\frac{1}{4}} \beta^{\frac{3}{4}}} \sum_{i=0}^{\infty} \frac{\gamma(\frac{i}{2} + \frac{1}{4}) \tilde{U}_i(V, \beta)}{(C_1 \beta)^{\frac{i}{2}}}, \quad \tilde{U}_i(V, \beta) = \frac{1}{(2i)!} \frac{d^{2i} e^{-\beta \tilde{U}_T}}{dx^{2i}}, \quad (25)$$

where identity was used

$$\int_{-\infty}^{\infty} e^{-\beta C_1 x^4} x^{2i} dx = \frac{1}{2} \frac{\gamma(\frac{i}{2} + \frac{1}{4})}{(C_1 \beta)^{\frac{i}{2} + \frac{1}{4}}},$$

Then using equations (7) one can obtain the desired EOS in the implicit form.

$$\begin{cases} p_T = -\frac{\Pi^{(5)}}{8\Pi^{(4)}} kT - A \frac{\Pi^{(7)}\Pi^{(4)} - \frac{3}{2}\Pi^{(5)}\Pi^{(6)}}{\Pi^{(4)\frac{5}{2}}} (kT)^{\frac{3}{2}} \\ E_T = \frac{3}{4} kT - A \frac{\Pi^{(6)}}{\Pi^{(4)\frac{3}{2}}} (kT)^{\frac{3}{2}}. \end{cases} \quad (26)$$

where  $A = \frac{\sqrt{3}\gamma(3/4)^2}{40\sqrt{2}\pi} \simeq 0.015$ . Solution of the system (26) shows that dependence  $p_T(E_T)$  has form

$$p_T = D_1 E_T + D_2 E_T^{\frac{3}{2}}. \quad (27)$$

On the other hand, the same dependence can be obtained by substituting  $f_1 = 0$  into equation (21).

$$p_T = -\frac{\Pi^{(3)}}{\sqrt{\lambda\Pi^{(4)}}} \sqrt{E_T}. \quad (28)$$

One can see that results given by equations (27) and (28) are qualitatively different even for the small thermal energy.

## 5 Exact EOS in the case of Morse potential

In case of a particular interatomic potential one can calculate the exact dependence of the thermal pressure on thermal energy using equations (8). Let us assume that particle interacts with walls by means of Morse potential.

$$\Pi = D(e^{-2\alpha(r-a)} - 2e^{-\alpha(r-a)}), \quad (29)$$

where  $D$  — bond energy,  $a$  — equilibrium distance,  $\alpha$  — parameter which characterizes the width of the potential well.

Then formulae (3) has the following form

$$\begin{aligned} U_0 &= 2D(e^{-2\nu} - 2e^{-\nu}) \\ U_T &= 2D(e^{-2\nu} \text{ch}(2\alpha x) - 2e^{-\nu} \text{ch}(\alpha x)) - U_0, \end{aligned} \quad (30)$$

where  $\nu = \alpha(b - a)$ . Substituting formula (30) into equations (8) one can obtain the dependence of thermal pressure and thermal energy on temperature.

The exact EOS for the case of Morse potential was derived in paper [12]. The approach proposed in [6], based on the particle dynamics method was used. Within

the scope of this approach the following dependence of thermal pressure on thermal energy was obtained

$$p_T = 2\alpha D \int_0^{z_m} \frac{[e^{-2\nu}\text{ch}(2z) - e^{-\nu}\text{ch}(z)] dz}{\sqrt{E - 2D [e^{-2\nu}\text{ch}(2z) - 2e^{-\nu}\text{ch}(z)]}} - 2\alpha D(e^{-2\nu} - e^{-\nu}), \quad (31)$$

$$z_m = \text{Arch} \left( \frac{e^\nu}{2} + \frac{\sqrt{e^{2\nu}(\frac{E_T}{D} + 1) + 2}}{2} \right), \quad E = E_T + 2D(e^{-2\nu} - 2e^{-\nu}).$$

In order to compare the predictions of equations (8) and (31) let us plot the dependence  $p_T(E_T)$ . The desired dependence for undeformed well  $b = a$  and for the case of critical deformation  $b = (1 + \ln 2/6)a \approx 1.1a$  is shown in figure 1. The value of parameter  $\alpha a$  was taken equal to 6. One can see that in case of undeformed

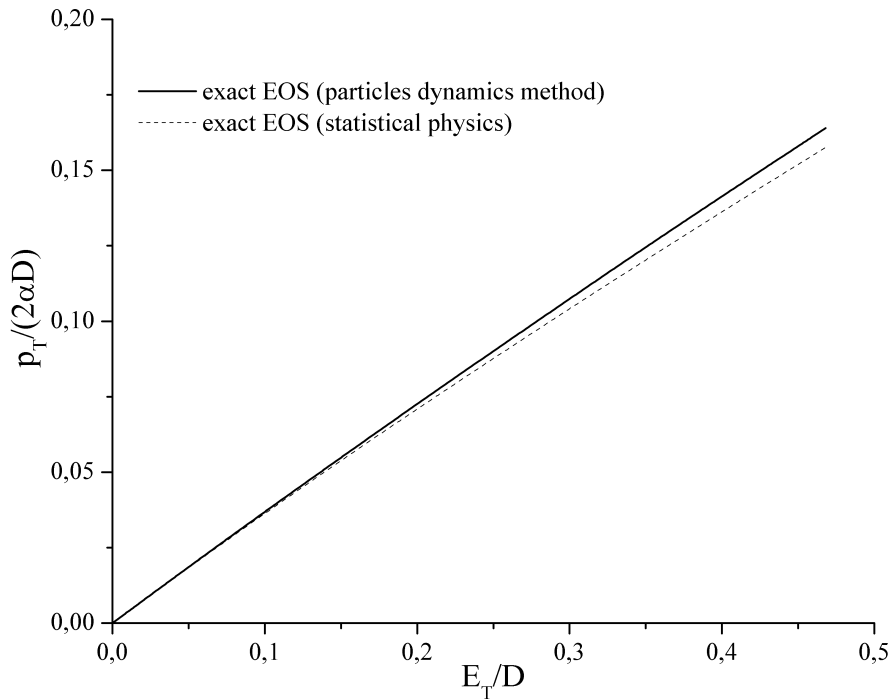


Figure 1: The dependence of thermal pressure on thermal energy in case of undeformed well ( $b = a$ ); circles — formula (8), squares — formula (31)

potential well the results of formulae (8), (31) are almost equal. However in case of critical deformation there is a differences about 10%. The comparison of the approximate EOS (26), (28) with the exact shows that the approximate EOS obtained by the methods of statistical physics is qualitatively different from the exact one.

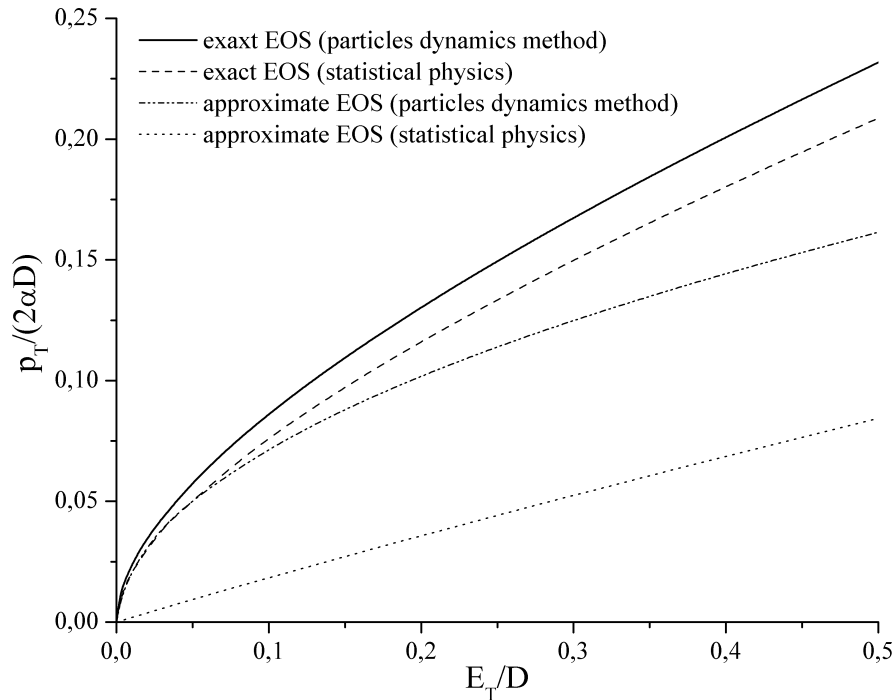


Figure 2: The dependence of thermal pressure on thermal energy in case of critical deformation well ( $b \approx 1.1a$ ); circles — formula (8), squares — formula (31)

## 6 Discussion

It can be seen in figures 1, 2 that there are essential differences between the results of the statistical physics approach and the exact solution. Let us note some “weak” places of the previous derivations. First of all, one can ask: “Is the statistical approach applicable to a single particle ?” The answer is: “No, it is not”. Motion of a single particle in the potential well is determined. From the formal point of view the expression for the statistical sum (4) loses sense because the total energy of the particle is constant and hence integral (4) is equal to infinity. However, one can consider the following model. The medium is represented by a large number of independent particles in the potential wells. The interactions between the particles are weak, so one can consider the behavior of a single particle. This approach solves the problem mentioned above. However, it is not the only problem. One can see that in all formulae for statistical sum ((4) et. all) the infinite limits on integral were used. Following the book [4] the integration is carried out by all phase space of the system. In the considered case coordinate of the particle is limited by the distance between walls. Therefore the limits on integrals should be equal to  $\pm b$ . However, the integrated function  $\exp(-\beta U(x))$  is rapidly decreasing with  $x$  for real potentials. Thus the use of the infinite limits can not lead to the serious errors.

Also let us note the difference between approximate and exact EOS obtained by methods of statistical physics. One can suppose that the reason is in the proposed method of approximation. However at least from the mathematical point of view all derivations are correct.



## 7 Conclusion

A simple model for elementary cell of 1D crystal was considered. The statistical approach was used. The new way of calculation of the statistical sum calculation was proposed. The expression for statistical sum in the form of a series with respect to temperature was obtained. In case of quasiharmonic approximation Mie–Gruneisen equation of state was derived. It was shown that the dependence of Gruneisen function on volume is similar to the prediction of paper [6]. The more precise equations of state were derived for different values of volume. It was shown that for both cases the equation of state is different from the results of paper [6]. The difference becomes principal in case of critical deformation of the potential well. Comparison of the results of statistical approach with the exact equation of state in case of Morse potential was carried out. It was shown that the results are close to each other for undeformed well. In case of critical deformation of the well 10% error was obtained. It was shown that approximate EOS obtained by the particle dynamics method is qualitatively equal to the exact one. In contrast approximate EOS obtained by the methods of statistical physics is qualitatively different from the exact one.

## 8 Appendix A

Let us consider functions  $U_i(V, \beta)$ . According to the definition (14) they have the following form

$$U_i(V, \beta) = \frac{1}{(2i)!} \frac{d^{2i}(e^{-\beta U_{ah}})}{dx^{2i}} \Big|_{x=0} \quad (32)$$

It can be shown that  $U_i(V, \beta)$  are polynomial functions with respect to  $\beta$ . Let us denote

$$u_{2i} = \frac{d^{2i}(e^{-\beta f(x)})}{dx^{2i}} \Big|_{x=0} \quad (33)$$

and carry out the following transformations

$$\begin{aligned} u_{2i} &= -\beta \frac{d^{2i-1}(f' e^{-\beta f})}{dx^{2i-1}} \Big|_{x=0} = -\beta \sum_{n=0}^{2i-1} C_{2i-1}^n f^{(n+1)} (e^{-\beta f})^{(2i-1-n)} \Big|_{x=0} = \\ &= -\beta \sum_{n=0}^{2i-1} C_{2i-1}^n f^{(n+1)} u_{2i-n-1} \Big|_{x=0}, \end{aligned} \quad (34)$$

where  $C_{2i-1}^n = \frac{n!(2i-1)!}{(2i-n-1)!}$ . One can see from equation (34) that  $u_{2i}$  are polynomials with respect to  $\beta$ . The degree of  $u_{2i}$  increases with increase of  $i$ . Let us determine the degree of  $u_{2i}$ . Let us assume  $f = U_{ah}$ . It has the following properties

$$f^{(i)}(0) = 0, \quad i = 0, 1, 2, 3. \quad (35)$$

Then equation (34) can be rewritten as

$$u_{2i} = -\beta \sum_{n=3}^{2i-1} C_{2i-1}^n f^{(n+1)}(0) u_{2i-n-1} \quad (36)$$

Let us denote the degree of  $u_{2i}$  as  $d_{2i}$ . Then one gets following equation for  $d_{2i}$

$$d_{2i} = d_{2i-4} + 1. \quad (37)$$

Solution of the last equation is  $d_{2i} = [i/2]$ , where  $[ ]$  denotes the integer part. Thus  $U_i(V, \beta)$  is a polynom of  $[i/2]$  degree with respect to  $\beta$ .

## References

- [1] V.A. Palmov, "Vibrations of Elastoplastic Bodies", Berlin, Springer-Verlag, Heidelberg, 1998.
- [2] P.A. Zhilin, "Mathematical theory of nonelastic media", Uspehi mehaniki. Vol. 2. No 4, 3–36, 2003 [in Russian].
- [3] S.B. Segletes, "Thermodynamic stability of the Mie-Grüneisen equation of state, and its relevance to hydrocode computations", J. Appl. Phys. V. 70, No 5, 2489–2499, 1990.
- [4] L.D. Landau, E.M. Lifshitz. Statistical physics. M.: Nauka, 1976.
- [5] V.N. Zharkov, V.A. Kalinin, "Equations of state for solids at high pressures and temperatures", Consultance Bureau, New York and London, 1971.
- [6] A.M. Krivtsov, "From nonlinear oscillations to equation of state in simple discrete systems", Chaos, Solitons & Fractals. V. 17. No. 1, 79–87, 2003.
- [7] A.M. Krivtsov, "Thermoelasticity of one-dimensional chain of interacting particles", Izvestiya vuzov. Severo-Kavkazskii region. Estestvennye nauki. Specvy-pusk. Nelineinye problemy mehaniki sploshnyh sred, 231–243, 2003 [in Russian].
- [8] A.M. Krivtsov. "Deformation and fracture of bodies with microstrure". M.: Physmatlit (2007). 304 p. [in Russian].
- [9] R.W. Hockney, J.W. Eastwood, "Computer simulation using particles", Taylor & Francis Group, New York, 1988.
- [10] A.M. Krivtsov, N.F. Morozov, "On Mechanical Characteristics of Nanocrystals", Physics of the Solid State, Vol. 44, No. 12, 2260–2265, 2002.
- [11] A.M. Krivtsov, "Molecular Dynamics Simulation of Plastic Effects upon Spalling", Physics of the Solid State, Vol. 46, No. 6, 1055–1060, 2004.
- [12] V. A. Kuzkin, A. M. Krivtsov, "Simple model for analytical derivation of equation of state for ideal crystals", Vestnik S.Pb. universiteta, Vol.1, No.3, p. 24–31, 2007. [in Russian]

- [13] A.S. Kondratiev, V.P. Romanov. *Zadachi po statisticheskoy phisike*, M.: Nauka, 1992.

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