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# From nonlinear oscillations to equation of state in simple discrete systems

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## Abstract

Nonlinear oscillations of a single particle in the potential well and for one-dimensional chain of interacting particles are considered. The law of interaction is of Lennard-Jones type, mimicking interaction in atomic systems. Similarities in average behaviour of the systems with one and many degrees of freedom are shown. Time averaging for the random oscillations is used to obtain thermodynamic characteristics such as pressure, specific volume, and thermal energy. Second order equation of state is obtained, which is valid in the conditions of strong extension, where fails the widely used Mie–Grüneisen equation of state.

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## 1. Introduction

Experimental [1] and computational [2,3] investigations show that random component of the velocities in a shock wave have a great influence on the impact strength of materials. At the mesoscopic scale level this component can be considered as the dispersion of mesoparticle velocities [1], and at the microscopic scale level it is tightly connected with the thermal energy and temperature. Unfortunately the fundamental laws leave too much freedom for the thermodynamic equation of state that is essential to close the system of the equations of motion in continuous media. This problem can be resolved by examining simple discrete systems, which allow to derive the equation of state directly, without phenomenological assumptions. Two such models are considered in the presented paper. The first model is a particle between two Lennard-Jones walls. Nevertheless this model has only one degree of freedom, it can be described by an equation of state in terms of pressure, volume and thermal energy. The advantage of this model is that derivation of the equation of state can be done rigorously. The second model is a periodic chain containing Lennard-Jones particles. This model has many degrees of freedom, but in the paper there will be shown that most of the equations, which are valid for the first model, can be also derived for the second one.

One of the widely used equations of state is the Mie–Grüneisen equation [4,5]

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

where the total pressure  $p$  is decomposed in two components. First one is the “cold” pressure  $p_0$ , which is a function of the specific volume  $V$  (quantity reverse to the density). The second one is the thermal pressure  $p_T$ , which is a function of the specific volume  $V$  and the specific thermal energy  $E_T$ . The dimensionless coefficient  $\Gamma(V)$  is the Grüneisen parameter, which depends on the specific volume only. Note, that only the statement that the Grüneisen coefficient does

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not depend on the thermal energy  $E_T$ , turns equation (1) from a simple identity to an equation of state. The concrete dependence of the Grüneisen coefficient on the specific volume is still a subject of debates, since the experimental data is usually not sufficiently complete. As a consequence, simple approximations, which are widely used in numeric computations, can lead to various instabilities and bring physically incorrect results [5]. The models being considered in the presented paper allow to obtain analytically the equation of state, which in the first approximation coincides with the Mie–Grüneisen equation of state, giving the explicit formula for the dependence of the Grüneisen coefficient on the specific volume.

In the presented paper the equation of state is obtained in the second approximation: two non-zero terms are left in the expansion of the thermal energy. This second approximation is usually considered as a small addition to the first one [4]. On contrary, the equation of state, which will be obtained further, is valid even when the first term in the expansion vanishes, so that the second term appears to be the main one in the expansion. This allows to obtain the equation of state, which is valid for the high tensile strains up to the tensile breakage. It will be shown that for such high strains the equation of state should be essentially different from the Mie–Grüneisen equation (1).

To obtain the equations of state the time averaging is used. This is close to the approach, which is used in the vibrational mechanics [6] and differs from the traditional approach in statistical physics, where the thermodynamic quantities are obtained via phase space averaging [4,7]. The time averaging in the considered case seems to be simpler from both mathematical and logical point of views, and also this kind of averaging can be easily computed by molecular dynamics method [2,3]. The use of the time averaging allows to limit our consideration in three thermodynamic quantities, namely pressure, volume, and thermal energy. These quantities are usually sufficient for describing fast impact processes, where the thermal conductivity can be neglected.

## 2. Particle in the potential well

### 2.1. Designations

Let us consider a particle in one dimension, constrained by two rigid walls. Equation of motion for the particle can be expressed in the form

$$m\ddot{x} = \Phi(x), \quad \Phi(x) \stackrel{\text{def}}{=} f(a+x) - f(a-x), \quad (2)$$

where  $f$  is the force of interaction between the particle and the wall,  $a$  is the half-distance between the walls,  $m$  is the mass of the particle,  $x$  is the coordinate of the particle. The origin for the  $x$  coordinate is the center position between the walls.

Let us denote potential of interaction between the particle and the wall as  $\Pi(r)$ , then  $\Pi'(r) = -f(r)$ . Denote the potential energy of the particle as  $U(x)$ :

$$U(x) \stackrel{\text{def}}{=} \Pi(a+x) + \Pi(a-x); \quad U'(x) = -\Phi(x). \quad (3)$$

The potential of interaction can be described by the Lennard-Jones law

$$\Pi(r) = D \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right], \quad (4)$$

where  $r_0$  is the equilibrium distance and  $D$  is the energy of interaction. The potential should not necessary be defined by formula (4), but it should possess the main features of this potential: repulsion at a short range (positive values), attraction at a long range (negative values), a single position of equilibrium, and so on. Morse potential, for example, is also acceptable.

### 2.2. Averaging

Let us introduce the averaging operator

$$\langle \mathcal{F} \rangle \stackrel{\text{def}}{=} \frac{1}{T} \int_0^T \mathcal{F}(t) dt, \quad (5)$$

where  $T$  is the period of the particle's oscillations. The following averaged characteristics will be used further

$$\kappa^2 \stackrel{\text{def}}{=} \langle x^2 \rangle, \quad \sigma^2 \stackrel{\text{def}}{=} \langle \dot{x}^2 \rangle. \quad (6)$$

Let us define the pressure as an average force between the particle and one of the walls

$$p \stackrel{\text{def}}{=} \langle f(a+x) \rangle \tag{7}$$

Then the cold and thermal pressure are

$$p_0 \stackrel{\text{def}}{=} f(a), \quad p_T \stackrel{\text{def}}{=} \langle f(a+x) - f(a) \rangle = p - p_0. \tag{8}$$

From the symmetry reasons  $\langle \ddot{x} \rangle \equiv 0$ , then from (2) it follows that

$$\langle f(a+x) \rangle \equiv \langle f(a-x) \rangle$$

and definitions (7), (8) can be rewritten as

$$p = \frac{1}{2} \langle f(a+x) + f(a-x) \rangle, \quad p_T = p - f(a). \tag{9}$$

Let us introduce thermal kinetic, potential, and total energies as following

$$\begin{aligned} K_T &\stackrel{\text{def}}{=} \left\langle \frac{1}{2} m \dot{x}^2 \right\rangle = \frac{1}{2} m \sigma^2, \\ U_T &\stackrel{\text{def}}{=} \langle U(x) - U(0) \rangle = \langle \Pi(a+x) + \Pi(a-x) \rangle - 2\Pi(a), \\ E_T &\stackrel{\text{def}}{=} K_T + U_T. \end{aligned} \tag{10}$$

The kinetic energy  $K_T$  can be expressed in terms of the interaction force using the following virial method

$$K_T = \frac{m}{2} \langle \dot{x}^2 \rangle = \frac{m}{2} \langle (x\dot{x})' - x\ddot{x} \rangle = \frac{m}{2T} x\dot{x} \Big|_0^T - \frac{1}{2} \langle x\Phi(x) \rangle. \tag{11}$$

Here definition (5) for the averaging operator and equation of motion (2) are used. Since  $T$  is the period of oscillations then the first term of the above equation is equal to zero, and finally we have the following analogue of the virial theorem

$$K_T = -\frac{1}{2} \langle x\Phi(x) \rangle = \frac{1}{2} \langle xf(a-x) - xf(a+x) \rangle. \tag{12}$$

Summarizing (10) and (12) the following formula for the total thermal energy can be obtained

$$E_T = \frac{1}{2} \langle xf(a-x) - xf(a+x) \rangle + \langle \Pi(a-x) + \Pi(a+x) \rangle - 2\Pi(a). \tag{13}$$

If  $x = x(t)$  is known as a solution of the equation of motion (2), then Eqs. (9) and (13) give an implicit representation of the desired equation of state  $p = p(E_T, V)$ , where the specific volume  $V$  is proportional to the distance  $a$ .

### 2.3. Expansion into power series

Let us expand the force  $f(a+x)$  into power series for small  $x$ :

$$f(a+x) = \sum_{k=0}^{\infty} (-1)^k f_k(a) x^k, \quad f_k(a) \stackrel{\text{def}}{=} (-1)^k f^{(k)}(a) / k!, \tag{14}$$

where  $f^{(k)}$  is the derivative of the order  $k$ . It can be shown that for the Lennard-Jones interaction each function  $f_k(a)$  has only one root  $r_k$ , the functions  $f_k(a)$  are positive for  $a < r_k$ , and the roots  $r_k$  form monotonically increasing sequence:  $r_0 < r_1 < r_2 < \dots$ . Note that  $r_0$  is the equilibrium distance for the interaction (4),  $r_1$  is the break distance (the distance at which the greatest value of the interaction force is realized). In particular, for the tensile deformations less than the break one:  $a < r_1$  all coefficients  $f_k(a)$  except  $f_0(a)$  are positive, and only the sign of  $f_0(a)$  can vary. Using (14) the interaction potential can be expanded as

$$\Pi(a+x) = \Pi(a) + \sum_{k=0}^{\infty} \frac{(-1)^{k+1}}{k+1} f_k(a) x^{k+1}. \tag{15}$$

Then using (9) and (13) the pressure and the total energy can be represented in the following form

$$p = \sum_{k=0}^{\infty} f_{2k}(a) \langle x^{2k} \rangle, \quad E_T = \sum_{k=0}^{\infty} \frac{k+2}{k+1} f_{2k+1}(a) \langle x^{2k+2} \rangle, \tag{16}$$

which is another implicit representation of the equation of state  $p = p(E_T, V)$ . The expansions for the kinetic and potential energies are

$$K_T = \sum_{k=0}^{\infty} f_{2k+1}(a) \langle x^{2k+2} \rangle, \quad U_T = \sum_{k=0}^{\infty} \frac{1}{k+1} f_{2k+1}(a) \langle x^{2k+2} \rangle. \quad (17)$$

#### 2.4. First approximation

Let us neglect the terms of the order higher than  $x^2$ . Then from (16) and (17) we obtain

$$p_T = f_2(a) \kappa^2, \quad E_T = 2f_1(a) \kappa^2; \quad K_T = U_T = E_T/2, \quad (18)$$

where  $\kappa^2 = \langle x^2 \rangle$ . Excluding  $\kappa^2$  from (18) the desired equation of state can be obtained

$$p_T = \frac{1}{2} \frac{f_2(a)}{f_1(a)} E_T. \quad (19)$$

The above equation can be represented in the Mie–Grüneisen form

$$p_T = \Gamma(a) \frac{E_T}{2a}, \quad \Gamma(a) \stackrel{\text{def}}{=} a \frac{f_2(a)}{f_1(a)}. \quad (20)$$

Here  $\Gamma(a)$  is the dimensionless Grüneisen coefficient,  $2a$  stands for the specific volume.<sup>1</sup> Unfortunately Eq. (19) is losing sense when  $a$  tends to  $r_1$ , which is the break distance for the interaction force. Indeed,  $f_1(a)$  in this case tends to zero, and hence the Grüneisen coefficient tends to infinity. The second approximation is required to correct this problem.

#### 2.5. Second approximation

Now let us leave the terms up to  $x^4$ . Then from (16) we obtain the second approximation for the pressure and the total energy

$$p_T = f_2 \langle x^2 \rangle + f_4 \langle x^4 \rangle, \quad E_T = 2f_1 \langle x^2 \rangle + \frac{3}{2} f_3 \langle x^4 \rangle. \quad (21)$$

Here and below  $f_k \equiv f_k(a)$ . The kinetic and potential energies are

$$K_T = f_1 \langle x^2 \rangle + f_3 \langle x^4 \rangle, \quad U_T = f_1 \langle x^2 \rangle + \frac{1}{2} f_3 \langle x^4 \rangle. \quad (22)$$

In the first approximation the kinetic and potential energies are equal—see (18). From (22) it follows that on contrary, in the second approximation, the kinetic energy is always greater than the potential one. Far from the break distance, for small amplitudes ( $x \ll 1$ ), the ratio  $K_T/U_T$  is indeed close to 1. However, while  $a$  tends to  $r_1$ , the ratio increases even for the small amplitudes, reaching the value of 2 at the break distance  $a = r_1$ .

The equation of state can not be obtained directly from (21), since this system contains two quantities to be excluded— $\langle x^2 \rangle$  and  $\langle x^4 \rangle$ . Of course, after solving the differential equation of motion (2) we can express both of these unknowns in terms of a single quantity, say amplitude of oscillations, which can then be excluded from system (21), giving finally the desired equation of state. But analytical solving of the equation of motion is a pretty complicated task, so it is desirable to find out method of solving (21) directly. This can be done using the following approximation

$$\langle x^4 \rangle = \lambda \langle x^2 \rangle^2 \equiv \lambda \kappa^4, \quad (23)$$

where  $\lambda \geq 1$  is a dimensionless coefficient, which is weakly dependent on  $a$ , at least for small amplitudes and  $a \leq r_1$ . The evidence of the approximate independence of  $\lambda$  on  $a$  can be obtained as following. If  $a$  is less then  $r_1$  and not close to  $r_1$ , then for small amplitudes the linear approximation for  $\Phi(x)$  in the equation of motion (2) is valid, which gives harmonic solution for  $x(t)$ , and then  $\lambda$  can be easily calculated

$$\lambda = \frac{\frac{1}{2\pi} \int_0^{2\pi} \sin^4(t) dt}{\left( \frac{1}{2\pi} \int_0^{2\pi} \sin^2(t) dt \right)^2} = \frac{3}{2} = 1.5. \quad (24)$$

<sup>1</sup> Formula  $V = 2a$  is obtained from the macroscopic relation  $p_0 = -\partial U_0 / \partial V$ , where  $U_0 \stackrel{\text{def}}{=} U|_{x=0}$ .

In the vicinity of  $a = r_1$  for small amplitudes the cubic approximation for  $\Phi(x)$  is required, since in this case  $\Phi'(x) \equiv 0$ . Solution in this case can be obtained in terms of elliptic functions, but much easier it can be calculated numerically, which gives  $\lambda \approx 1.59642 \approx 1.6$ . Thus for  $a \leq r_1$  the difference between  $\lambda$  and  $3/2$  is not more than 7%. This proves that coefficient  $\lambda$  in (23) can be approximately considered as a constant. Now system (21) can be rewritten in the form

$$p_T = f_2 \kappa^2 + \lambda f_4 \kappa^4, \quad E_T = 2f_1 \kappa^2 + \frac{3}{2} \lambda f_3 \kappa^4. \tag{25}$$

Excluding  $\kappa$  from the above system one can obtain the desired equation of state. If we will limit our consideration to the case when  $f_2$  is not small, which is obviously fulfilled for  $a \leq r_1$ , then the second term for  $p_T$  in the above formula can be neglected, which will give finally the following equation of state

$$p_T = f_2(a) \frac{\sqrt{f_1^2(a) + \frac{3}{2} \lambda f_3(a) E_T} - f_1(a)}{\frac{3}{2} \lambda f_3(a)}. \tag{26}$$

Let us note that this equation of state is absolutely different from the Mie–Grüneisen one. Even more visible it is in the case when  $a$  is close to  $r_1$ , then  $f_1$  in the above formula can be neglected, which gives

$$p_T = f_2(a) \sqrt{\frac{2E_T}{3\lambda f_3(a)}}. \tag{27}$$

This is the equation of state in the vicinity of the bond breakage. The thermal pressure in this equation is proportional to the square root of the thermal energy. Remind that according to the Mie–Grüneisen equation of state the thermal pressure should be proportional to the first degree of the thermal energy.

### 3. One-dimensional chain

#### 3.1. Designations

Consider longitudinal oscillations in one-dimensional chain containing equal particles interacting via an interparticle force of the Lennard-Jones type. Let us limit our consideration to the case when each particle interacts only with two nearest neighbors. The equation of motion for the particles can be expressed in the form

$$m\ddot{u}_n = \Phi_n, \quad \Phi_n \stackrel{\text{def}}{=} F_n - F_{n+1}, \quad F_n = f(a + \Delta_n), \quad \Delta_n \stackrel{\text{def}}{=} u_n - u_{n-1}, \tag{28}$$

where  $u_n$  is the particle's displacement;  $F_n$  is the force, acting on the particle  $n$  from the particle  $n - 1$ ; the function  $f$  is the interaction force;  $a$  is the equilibrium distance between the particles in the chain. Note that in general the equilibrium force between the particles is not zero and the equilibrium distance is not  $r_0$ . We will apply periodical conditions  $u_{n+N} \equiv u_n$ , where  $N$  is number of independent particles in the chain.

#### 3.2. Averaging

Let us introduce the averaging operator

$$\langle \mathcal{F} \rangle \stackrel{\text{def}}{=} \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \mathcal{F}(t) dt. \tag{29}$$

We will consider only the states of the chain when any averaged characteristic does not depend on the particle number  $n$ . The averaged quantities analogous to (6), (7) are

$$\kappa^2 \stackrel{\text{def}}{=} \langle \Delta_n^2 \rangle, \quad \sigma^2 \stackrel{\text{def}}{=} \langle \dot{u}_n^2 \rangle, \quad p \stackrel{\text{def}}{=} \langle F_n \rangle, \tag{30}$$

where  $p$  will be called as the pressure in the chain. Let us introduce the specific thermal energies corresponding to a single particle as following

$$K_T \stackrel{\text{def}}{=} \left\langle \frac{1}{2} m \dot{u}_n^2 \right\rangle = \frac{1}{2} m \sigma^2, \quad U_T \stackrel{\text{def}}{=} \langle \Pi(a + \Delta_n) - \Pi(a) \rangle, \quad E_T \stackrel{\text{def}}{=} K_T + U_T, \tag{31}$$

where  $K_T$ ,  $U_T$ , and  $E_T$  are the kinetic, potential, and total energy, respectively.

If we accept that the displacements and velocities of the particles are bounded, then the virial theorem can be applied (similarly to (11)), that gives the following representation for the kinetic energy

$$K_T = -\frac{1}{2}\langle\Phi_n u_n\rangle. \quad (32)$$

The right-hand side of the above formula can be modified as following

$$\langle\Phi_n u_n\rangle = \langle F_n u_n\rangle - \langle F_{n+1} u_n\rangle = \langle F_n u_n\rangle - \langle F_n u_{n-1}\rangle = \langle F_n \Delta_n\rangle, \quad (33)$$

where identity  $\langle F_{n+1} u_n\rangle \equiv \langle F_n u_{n-1}\rangle$  is used, which is consequence from the statement that any averaged characteristic does not depend on  $n$ . Substitution (33) to (32) gives finally

$$K_T = -\frac{1}{2}\langle F_n \Delta_n\rangle. \quad (34)$$

### 3.3. Expansion into power series

Using expansion (14) for the interaction force the pressure (30) can be represented in the following form

$$p = \langle f(a + \Delta_n)\rangle = \sum_{k=0}^{\infty} (-1)^k f_k(a) \langle \Delta_n^k \rangle = \sum_{k=0}^{\infty} f_{2k}(a) \langle \Delta_n^{2k} \rangle. \quad (35)$$

From the symmetry reasons the average of the odd powers in the above equations were accepted to be zero. The cold and thermal pressure can be calculated as following

$$p_0 \stackrel{\text{def}}{=} f(a), \quad p_T \stackrel{\text{def}}{=} \langle f(a + \Delta_n) - f(a) \rangle = p - p_0. \quad (36)$$

By the same way, as it was done for the pressure, one can obtain from (34)

$$K_T = \frac{1}{2} \sum_{k=0}^{\infty} (-1)^{k+1} f_k(a) \langle \Delta_n^{k+1} \rangle = \frac{1}{2} \sum_{k=0}^{\infty} f_{2k+1}(a) \langle \Delta_n^{2k+2} \rangle. \quad (37)$$

Potential energy  $U_T$  defined by (31) can be calculated with the use of expansion (15)

$$U_T = \sum_{k=0}^{\infty} \frac{(-1)^{k+1}}{k+1} f_k(a) \langle \Delta_n^{k+1} \rangle = \frac{1}{2} \sum_{k=0}^{\infty} \frac{1}{k+1} f_{2k+1}(a) \langle \Delta_n^{2k+2} \rangle. \quad (38)$$

Thus the pressure and the total energy take the form

$$p = \sum_{k=0}^{\infty} f_{2k}(a) \langle \Delta_n^{2k} \rangle, \quad E_T = \frac{1}{2} \sum_{k=0}^{\infty} \frac{k+2}{k+1} f_{2k+1}(a) \langle \Delta_n^{2k+2} \rangle, \quad (39)$$

which can be interpreted as an implicit representation of the equation of state, similar to the one we had for the single particle, formulae (16). The slight difference is the coefficient 1/2 in the formula (39) for  $E_T$ . This coefficient appears because the amount of particles and interparticle forces is equal in the case of the periodic chain, but in the case of the single particle there are two interaction forces (with two walls) for one particle. Let us also summarize the expansions for the kinetic and potential energies

$$K_T = \frac{1}{2} \sum_{k=0}^{\infty} f_{2k+1}(a) \langle \Delta_n^{2k+2} \rangle, \quad U_T = \frac{1}{2} \sum_{k=0}^{\infty} \frac{1}{k+1} f_{2k+1}(a) \langle \Delta_n^{2k+2} \rangle. \quad (40)$$

### 3.4. First approximation

Neglecting the terms of the order higher than  $\Delta_n^2$ , one can obtain

$$p_T = f_2(a) \kappa^2, \quad E_T = f_1(a) \kappa^2; \quad K_T = U_T = E_T/2, \quad (41)$$

where  $\kappa^2 = \langle \Delta_n^2 \rangle$ . The corresponding equation of state is

$$p_T = \frac{f_2(a)}{f_1(a)} E_T = \Gamma(a) \frac{E_T}{a}; \quad \Gamma(a) \stackrel{\text{def}}{=} a \frac{f_2(a)}{f_1(a)}. \quad (42)$$

Here  $\Gamma(a)$  is the dimensionless Grüneisen coefficient,  $a$  stands for the specific volume. The above formula for the Grüneisen coefficient coincides with the formula, obtained by another way in [7], where the similar periodic chain is considered. As it was for the single particle (19), the above equation becomes incorrect when  $a$  tends to the break distance  $r_1$ , and hence the second approximation is required in the vicinity of the break area.

### 3.5. Second approximation

The second approximation for the pressure and the total energy is

$$p_T = f_2 \langle A_n^2 \rangle + f_4 \langle A_n^4 \rangle, \quad E_T = f_1 \langle A_n^2 \rangle + \frac{3}{4} f_3 \langle A_n^4 \rangle. \quad (43)$$

The kinetic and potential energies are

$$K_T = \frac{1}{2} f_1 \langle A_n^2 \rangle + \frac{1}{2} f_3 \langle A_n^4 \rangle, \quad U_T = \frac{1}{2} f_1 \langle A_n^2 \rangle + \frac{1}{4} f_3 \langle A_n^4 \rangle. \quad (44)$$

All conclusions about the relations between the kinetic and potential energies obtained for the case of the single particle can be applied for the chain. Namely, for  $a \leq r_1$  it holds that  $U_T < K_T \leq 2U_T$ . If  $a$  is not close to  $r_1$ , then for small amplitudes  $K_T \approx U_T$ . In the vicinity of  $r_1$  even for the small amplitudes  $K_T \approx 2U_T$ .

To obtain equation of state from (43) let us use the assumption similar to (23):

$$\langle A_n^4 \rangle = \lambda \langle A_n^2 \rangle^2 \equiv \lambda k^4, \quad (45)$$

where  $\lambda \geq 1$  is a dimensionless coefficient, which is weakly dependent on  $a$ , at least for small amplitudes and  $a \leq r_1$ . Proof of this statement for the case of the chain is much more complicated than for the case of the single particle, since value of  $\lambda$  can depend on the distribution of displacements and velocities in the chain. The other important feature that differs the chain from the single particle is that the even terms in the expansions of the equations of motion are not identically zeros. Hence the second term in the force expansion can affect the value of  $\lambda$ . Computations show that for the following two types of uniform initial distributions  $-u_{\max} < u_n < u_{\max}$ ,  $v_n \equiv 0$  and  $u_n \equiv 0$ ,  $-v_{\max} < v_n < v_{\max}$  in a linear chain the value of  $\lambda$  is equal to 3 with a good accuracy—error is not more than 1%. If the square terms are left in the force expansion then the result is different for these two distributions, but the value of  $\lambda$  can still be taken as 3 approximately, were the error is not more than 13%. Account of the cubic terms can even increase this error, but still assumption (45) can be used as a more or less accurate approximation. Then, using (43), (45) and analogy with (26), one can get the following equation of state

$$p_T = 2f_2(a) \frac{\sqrt{f_1^2(a) + 3\lambda f_3(a)E_T} - f_1(a)}{3\lambda f_3(a)}. \quad (46)$$

Let us remind that for the simplicity reasons in the derivation of the above equation the second term was neglected in the formula for  $p_T$  (43). This does not give big error, since for  $a \leq r_1$  in the expansion of  $p_T$  the second term is always small with respect to the first one (on contrary, in the expansion of  $E_T$  both terms can be valuable). In the vicinity of the break distance equation (46) reduces to

$$p_T = 2f_2(a) \sqrt{\frac{E_T}{3\lambda f_3(a)}}. \quad (47)$$

Exactly as it was for the case of the single particle, the above equation of state disagrees with the Mie–Grüneisen equation of state.

Generally, equation (46) is valid for  $a \leq r_1$ . For the greater values of  $a$  it might fail for a number of reasons. The main of them is that the symmetry assumptions can fail for  $a > r_1$  due to instability of the symmetric equilibrium. But for some certain conditions this equation can be extended up to the vicinity of  $r_2$ , where the second term in the expansion of  $p_T$  (43) should be accounted for.

### 3.6. Dispersion

Dispersion of the particle's velocities,  $\sigma^2$ , plays an important role in impact fracture processes [1,2]. Generally it is defined as following

$$\sigma^2 \stackrel{\text{def}}{=} \overline{(v_n - \bar{v}_n)^2} = \bar{v}_n^2 - \bar{v}_n^2, \quad (48)$$

where the lines over the quantities mean averaging among all particles in some space region:

$$\overline{\mathcal{F}_n} \stackrel{\text{def}}{=} \frac{1}{N} \sum_{n=1}^N \mathcal{F}_n. \quad (49)$$

Let us apply averaging (49) for the case of the periodic chain, considering  $N$  as the number of the independent particles in the chain. Let us show that then definitions (30) and (48) define the same quantity  $\sigma^2$ . From one hand side, as it was stated above, result of the time averaging (29) should not depend on  $n$ . From other hand side, if  $n$  is sufficiently big then for thermodynamically equilibrium states (in which we shall limit our consideration) the result of space averaging (49) should not depend on time. Then one can obtain

$$\begin{aligned} \langle \mathcal{F}_n(t) \rangle \text{ does not depend on } n &\Rightarrow \langle \mathcal{F}_n(t) \rangle \equiv \overline{\langle \mathcal{F}_n(t) \rangle}, \\ \overline{\mathcal{F}_n(t)} \text{ does not depend on } t &\Rightarrow \overline{\mathcal{F}_n(t)} \equiv \langle \overline{\mathcal{F}_n(t)} \rangle. \end{aligned} \quad (50)$$

But since space averaging operator (49) is a simple sum, then the order of the time and space averaging does not affect the result:

$$\overline{\langle \mathcal{F}_n(t) \rangle} \equiv \langle \overline{\mathcal{F}_n(t)} \rangle \quad (51)$$

and then from (50) it immediately follows, that results of the time and space averaging are equal. Then, keeping in mind that in our case  $\langle v_n \rangle \equiv 0$ , we can clearly see that definitions (30) and (48) define the same quantity  $\sigma^2$ , further called as dispersion.

Accordingly to its definition, the dispersion is always proportional to the thermal kinetic energy:  $m\sigma^2 \equiv 2K_T$ . Accordingly to (41), in the first approximation the dispersion is proportional to the total thermal energy and can replace it in equation of state (42)

$$E_T = m\sigma^2, \quad p_T = \frac{f_2(a)}{f_1(a)} m\sigma^2 = \frac{m}{a} \Gamma(a) \sigma^2. \quad (52)$$

On contrary, in the second approximation the dispersion is not proportional to the thermal energy. Their relation can be obtained from (43), (44) with the use of (45)

$$E_T = f_1 \kappa^2 + \frac{3}{4} \lambda f_3 \kappa^4, \quad m\sigma^2 = f_1 \kappa^2 + \lambda f_3 \kappa^4. \quad (53)$$

From the above equations it follows that for  $a \leq r_1$

$$\frac{3}{4} m\sigma^2 \leq E_T < m\sigma^2, \quad (54)$$

where the lower bound can be reached at the break distance  $a = r_1$ . The explicit representation of the total thermal energy in terms of the dispersion is

$$E_T = \frac{3}{4} m\sigma^2 + \frac{f_1}{8\lambda f_3} \left( \sqrt{f_1^2 + 4\lambda f_3 m\sigma^2} - f_1 \right). \quad (55)$$

The equation of state, corresponding to (46), in terms of the dispersion is

$$p_T = f_2 \frac{\sqrt{f_1^2 + 4\lambda f_3 m\sigma^2} - f_1}{2\lambda f_3}. \quad (56)$$

#### 4. Conclusions

Two simple systems were considered, namely a particle in the potential well and the periodic chain. Equations of state for both of them were obtained. During the derivation the thermal pressure and energy were expanded into power series in terms of the small vibrational parameter, and only the main terms were left in the equations of state. The obtained equations are valid up to the break tensile deformations. The equations of state for both systems are nearly equal, the difference is only in the multiplier with the thermal energy. If tensile deformations are not very strong, then the obtained equations are close to the Mie–Grüneisen equation of state. But when the system approaches the break deformation, then it appears that the Mie–Grüneisen equation is not valid, since the Grüneisen coefficient tends to infinity. In this case the second term in the power expansions of the thermal energy should be left. Use of this second



approximation gives the equation of state, which differs from the Mie–Grüneisen equation. This difference is small if the chain is free or compressed. But if the chain is stretched, then the difference became greater, obtaining its maximum value in the vicinity of the break extension.

The Mie–Grüneisen equation of state is widely used in numeric computations, especially for investigations of bodies impacting at high velocities. It is the main working equation of state in the hydrodynamic wave codes for various computer packages, such as MESA [8], DYNA [9] and others. The presented investigations show that the Mie–Grüneisen equation of state can fail for the processes where high tensile deformations appear. As the great tensile deformations are the initiator of the spallation processes, from the presented investigations it follows that the Mie–Grüneisen equation of state can have problems in describing spallation, especially in the zone of the spall fracture. In general, any impact processes where fracture is involved, could be problematic for the Mie–Grüneisen equation of state.

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