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Equilibrium thermodynamics and thermodynamic processes in nonlinear systems

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Abstract. A general method for the calculation of thermodynamic quasi-equilibrium processes by molecular dynamics (MD) simulation in canonical ensemble is developed. The method is suitable for classical systems with arbitrary interaction potentials. Though this MD method does not allow to calculate directly partition function and entropy, it is possible to calculate necessary partial derivatives which enter into the expressions for the full derivatives dT/dV and $d\beta/dV$ for adiabatic and isobaric processes. Namely the solutions of these ordinary differential equations define the corresponding thermodynamic processes. The adiabatic process for the 1D Toda lattice is analyzed in details. The usage of the Toda potential allows to perform all analytical calculus up to accurate answers and to compare numerical and analytical results. Exact analytical expressions for the thermodynamics of 1D lattices with few types of nearest neighbor interactions are obtained as a necessary interim solutions. MD-simulation of quasi equilibrium processes in canonical ensemble demands the achievement of thermodynamic equilibrium, thus the thermalization kinetics is briefly discussed.

PACS. 05.70.–a Thermodynamics – 05.50.+q Lattice theory and statistics

1 Introduction

The celebrated paper of Fermi-Pasta-Ulam (FPU) [1] initiated several new directions in the nonlinear physics: numerical experiment, soliton dynamics, chaos theory and others. The primary goal of FPU was to the use of computers to study the fundamental questions on the foundations of statistical mechanics

The dynamical properties of nonlinear systems in microcanonical ensemble (total energy $E = \text{const.}$) are thoroughly analyzed in most papers. It allows to investigate the dynamics and to get exact results (soliton [2–4] and breather [5–9] solutions), to analyze regular and stochastic regimes and to find the corresponding thresholds (for more details see reviews in special issues of journals *Chaos* [10] and *Lecture Notes in Physics* [11] devoted to the 50th anniversary of the FPU preprint).

Thermodynamics was also investigated. Feynman got an analytical expressions [12] for the 1D gas of repulsive particles with the potential $u(y) = \exp(-|y|)$. Toda constructed the thermodynamics for the 1D lattice of particles interacting via the potential $u(y) = (a/b) \exp(-by) + ay$ [13]. The thermodynamic of a one-dimensional model

system was calculated by the functional integral methods [14]. For a one-dimensional fluid model with the pair interaction potential of a hard core and the exponential attraction it was found a phase transition described exactly by the van der Waals equation [15].

Other methods were also advanced for more complex systems, examples are the Bethe Ansatz [16–18], and the modulation theory [19]. Several different approaches are also known [20–24]. The thermodynamics of the on-site Morse potential can be treated exactly in the continuum limit [25]. Analytical expressions for correlation functions are derived; and numerical transfer-integral values obtained for a discrete version of the model.

Recently we investigated one-dimensional (1D) lattices with Toda and Morse potentials in the microcanonical (T, L) ensemble [26,27] (L – lattice length). The lattices with constant energies and deformations were considered, and the temperature T and force F were found both analytically and numerically. But a few problems were found in the numerical microcanonical simulation.

Firstly, the thermal equilibrium achievement requires a rather long-time. Secondly, the averaging should be done over large number of MD-trajectories, i.e. many different initial conditions should be tested. Nevertheless, it does not guarantee that the initial conditions cover all phase

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space. Thirdly, very large (non-physical) fluctuations of energy were detected during the deformation of the lattice. This unexpected result is probably related to the computational “noise”. Chirikov was the first who pointed to this possibility [28].

An advantage of the canonical ensemble simulation is the absence of necessity to analyze the ergodic properties: any initial condition sooner or later results in the Gibbs distribution. If the thermostat is simulated by the Langevin sources then it can be proven that the Fokker–Planck equation gives the equilibrium Gibbs distribution at $t \rightarrow \infty$.

The paper is organized as follows. The analytical expressions for the equilibrium thermodynamic variables (partition function, entropy and others) for the 1D lattices with Toda’s exponential, Morse, and β -FPU potentials of interactions for the neighboring particles in the canonical (V, T) ensemble are derived in Section 2. In the next section we advance a new method which allows to perform the MD-simulation of adiabatic and isobaric processes for arbitrary classical systems. Analytical results are obtained for the 1D Toda’s exponential repulsive potential which allow to compare numerical and analytical results. The MD simulation of adiabatic process for the Toda lattice is presented in Section 4. Numerical calculations in canonical ensemble imply an achievement of equilibrium state (thermalization). The thermalization rates of different values to equilibrium are briefly considered in Appendix B. Thermodynamics of Toda’s lattice in (P, T) ensemble is considered in Appendix A.

2 Equilibrium thermodynamics of 1D nonlinear lattices in canonical ensemble

2.1 Generic types of potentials

Below we derive general expressions for the thermodynamic variables for (L, T) ensemble for the arbitrary potentials of interparticle interactions in the canonical ensemble. An analogous problem was successfully solved by Toda in the (P, T) ensemble for the potential $u(y) = (a/b) \exp(-by) + ay$ [13]. The dimensionless potential will be used below. Then in addition to energy $[a/b]$, length $[1/b]$, force $[a]$ and mass $[m]$ units, unit of time is $[t] = \sqrt{m/(ab)}$. Temperature is also measured in energy units, i.e. $k_B = 1$.

The 1D lattice of N particles with the potential interaction of nearest neighbors $u(x_{i+1} - x_i)$ depending on the relative displacements of particles from their equilibrium positions is considered below. The conjugated thermodynamic variables in canonical ensemble in the 1D case are temperature T and lattice length L . The constant (on average) temperature of the system is maintained by the heat bath. The constant lattice length is fixed by rigid boundary conditions $x_0 = 0$ and $x_{N+1} = L$. Specific deformation is $\varepsilon = L/(N+1)$, and it is also the absolute deformation of one bond. Hence, we consider the (L, T) ensemble in contrast to the Toda’s force–temperature ensemble.

The partition function is $Z = \int d\Gamma \exp(-\beta U)$, where U is the sum of kinetic (U_k) and potential ($U_p = \sum_{i=1}^{N+1} u(x_i - x_{i-1})$) energies. In the canonical ensemble the partition function Z can be expressed through the product of “coordinate” (related to potential energy) and “velocity” (related to kinetic energy) partition functions [29]

$$Z = Z_x Z_v = \int d\Gamma_x \exp(-\beta U_p) \int d\Gamma_v \exp(-\beta U_k);$$

$$\beta = 1/T, \quad k_B = 1, \quad (1)$$

where $Z_v = (2\pi/\beta)^{N/2}$. The partition function Z_v depends only on temperature and it should be taken into account only if derivatives with respect to temperature are necessary; it can be neglected in other cases.

As is well known, the partition function can be reduced to the one-dimensional integral using the Fourier transformation of the potential energy [13]. But it is more convenient to utilize the complex Fourier transformation

$$g(z) = \int \exp(-zx) \exp[-\beta u(x)] dx; \quad (z = a + ik). \quad (2)$$

Then the partition function for the lattice at arbitrary specific deformations ε can be expressed through $g(z)$

$$Z_x = \frac{1}{2\pi i} \int [g(z) \exp(\varepsilon z)]^{N+1} dz, \quad (3)$$

where integration can be performed along *any* line $\text{Re } z = a > 0$ in the complex plane.

The knowledge of partition function allows to calculate all necessary thermodynamical variables. An expression for the mean value of specific potential energy is

$$\frac{\langle U_p \rangle}{N+1} = [(N+1)Z_x]^{-1} \int d\Gamma_x U_p \exp(-\beta Z_x)$$

$$= -\frac{1}{2\pi i Z_x} \int \frac{\partial \ln g(z)}{\partial \beta} [g(z) \exp(\varepsilon z)]^{N+1} dz. \quad (4)$$

This value can be also obtained by numerical differentiation of expression (3) for the partition function: $\langle U_p \rangle = -\partial \ln Z_x / \partial \beta$; ($\langle \dots \rangle$ stand for the thermodynamic mean values (ensemble average) of the corresponding thermodynamic function, e.g. $\langle U_p \rangle = Z_x^{-1} \int U_p \exp(-\beta Z_x) d\Gamma$).

An expression for the entropy can be obtained as follows. The free energy is $A = -T \ln Z$. From the thermodynamic identity $A = \langle U \rangle - TS$ one gets $S = (\langle U_p \rangle + \langle U_k \rangle) / T + \ln Z_x + \ln Z_v$. In the canonical ensemble holds $\langle U_k \rangle \equiv NT/2$. And, omitting unessential numerical summands, the expression for the entropy reads

$$S = \langle U_p \rangle / T + \ln Z_x + N \ln T / 2. \quad (5)$$

An integral expression for the entropy can be obtained by substitution of (4) for $\langle U_p \rangle$ and (3) for Z_x in (5).

Now we derive the expression for the pressure $\langle F \rangle$ (actually $\langle F \rangle$ is the force acting on the right end of the 1D lattice and $\langle F \rangle = \langle F_{N+1} \rangle$, where $F_i = -u'_{x_i}(x_i - x_{i-1})$)

is the force acting on the $(i + 1)$ th particle from left to right). This value is also defined as $\langle F \rangle = T \partial S / \partial L$, and differentiation of S gives

$$\langle F \rangle = T Z_x^* / Z_x, \quad \text{where} \quad (6)$$

$$Z_x^* = \frac{1}{2\pi i} \int z [g(z) \exp(\varepsilon z)]^{N+1} dz. \quad (7)$$

2.2 Thermodynamics of the 1D lattice with exponential potential

As an example we consider the lattice of N particles with the dimensionless exponential potential $u(y_i) = \exp(-y_i)$, ($y_i = x_i - x_{i-1}$) for the particles interaction. Rigid boundaries ($x_0 = 0$, $x_{N+1} = L$) ensure fixed length L and lattice stability for this repulsive potential. This potential differs from the commonly used Toda potential $u^T(y) = \exp(-y) + y$ by an absence of the linear term.

The choice of the exponential potential is done by two reasons. The first one is its simple analytical form which allows to perform necessary analytical calculations. In the case of exponential potential with rigid boundaries the total potential energy is the sum of $(N + 1)$ energies of bonds between particles

$$U_p = \exp(-x_1) + \exp[-(x_2 - x_1)] + \dots + \exp[-(x_N - x_{N-1})] + \exp[-(L - x_N)]. \quad (8)$$

If the Toda potential $u^T(y) = \exp(-y) + y$ is used then $U_p^T = \sum_i \exp(-y_i) + L$ what differs from (8) by the summand L . In the thermodynamic limit the role of this summand is negligible but all formulae become more complex. This is another reason for the choice of the exponential potential. Additional advantage of the exponential potential is the ability to compare the numerical and analytical results.

Expressions (3)–(6) are valid for arbitrary nearest neighbor potentials, but they can be considerably simplified for the exponential potential. The transformation (2) for this potential is $g(z) = T^z \Gamma(z)$, where Γ – gamma-function. All necessary variables (Z_x , S , $\langle U_p \rangle$, $\langle F \rangle$) can be expressed through three integrals Z_k ($k = 0, 1, 2$)

$$Z_k = \frac{1}{2\pi i} \int z^k [\Gamma(z) \alpha^z]^{N+1} dz, \quad (9)$$

where $\alpha = T \exp(\varepsilon)$. One can check that

$$\langle U_p \rangle = (N + 1) T Z_1 / Z_0; \quad (10)$$

$$S = (N + 1) Z_1 / Z_0 + \ln Z_0 + (N \ln T) / 2; \quad (11)$$

$$\langle F \rangle = T Z_1 / Z_0. \quad (12)$$

Note, that Z_0 depends only on one variable α . This allows to derive the relation between the force $\langle F \rangle$ and the ensemble average of potential energy $\langle U_p \rangle$. Actually $\langle F \rangle = T \frac{\partial \ln Z_0}{\partial L} = \frac{\alpha T}{N + 1} \frac{\partial \ln Z_0}{\partial \alpha}$, and $\langle U_p \rangle = -\frac{\partial \ln Z_0}{\partial \beta} = \alpha T \frac{\partial \ln Z_0}{\partial \alpha}$. And the comparison

of these expressions for $\langle F \rangle$ and $\langle U_p \rangle$ gives the “equation of state” for the exponential lattice

$$\langle F \rangle = \langle U_p \rangle / (N + 1). \quad (13)$$

This expression can be derived less formally. For the exponential potential the forces between any pair of particles are equal on average and $F = -u' = u = U_p / (N + 1)$ and (13) immediately follows after thermodynamic averaging.

Note, that all integrals (3), (4), (7), (9) can be numerically calculated along any line $\text{Re } z = a > 0$ in the complex plane. But the integrand strongly oscillates at arbitrary $\text{Re } z$, what makes the calculation difficult and inaccurate. The most effective integration path goes through the saddle point, where the integrand has the Gaussian shape. The saddle point and the corresponding z value can be found from the solution of the equation $g'(z) + \varepsilon g(z) = 0$. The comparison of results for the exponential potential with those obtained by M. Toda is presented in Appendix A.

Additionally, we derive analytical expressions for the transformation (2) which allow to calculate all thermodynamic variables in the (L, T) ensemble for Morse and β -FPU potentials. The transformation (2) for the dimensionless Morse potential $u(y) = [1 - \exp(-y)]^2$ is represented as a series

$$g(z) = \frac{\exp(\varepsilon z - \beta)}{2 \beta^{z/2}} \sum_{k=0}^{\infty} \Gamma\left(\frac{z+k}{2}\right) \frac{(2\sqrt{\beta})^k}{k!} \quad (14)$$

and all thermodynamic expressions (3)–(6) are valid.

For the β -FPU potential $u(y) = y^2/2 + y^4/4$ the partition function Z_x (3) in the limit $N \rightarrow \infty$ can be estimated as $Z_x \approx g(0)^{N+1}$ as $g(z)$ has a sharp maximum at $z = 0$. There exists a simple analytical expression for $g(0)$:

$$g(0) = 2^{-1/2} \exp(w) K_{1/4}(w), \quad (15)$$

where $w = \beta/8$ and $K(\dots)$ – modified Bessel function.

The following expression for the specific potential energy can be obtained in the thermodynamic limit $N \rightarrow \infty$

$$\frac{\langle U_p \rangle}{N} = -\frac{\partial}{\partial \beta} \ln g(0) = \frac{1}{8} \left[\frac{K_{5/4}(w) + K_{3/4}(w)}{2 K_{1/4}(w)} - 1 \right]. \quad (16)$$

More accurate result for the partition function can be obtained if the preexponential multiplier as taken into account in the saddle-point evaluation of the corresponding integral. Then one gets

$$Z_x \approx \frac{1}{2\pi} g(0)^{N+1} \sqrt{\frac{2\pi g(0)}{-g''(0)(N+1)}} \quad (17)$$

with an expression for $g''(0)$:

$$g''(0) = \frac{1}{2} (2/\beta)^{1/4} \exp(w) \left\{ K_{1/4}(w) \left[w^{1/4} + \frac{1}{4} w^{-3/4} \right] - \frac{1}{2} w^{1/4} [K_{5/4}(w) + K_{3/4}(w)] \right\}. \quad (18)$$

3 Thermodynamic processes

Integral expressions for thermodynamic variables for three model systems are obtained in the previous section. Few of them ($\langle U_p \rangle, \langle F \rangle$) can be easily found in MD-simulations. Some quasi-equilibrium thermodynamic processes, e.g. isothermal and isochoric, can be also easily simulated by the MD method. For example, slow length change in isothermal process gives necessary force variation. The constant temperature can be maintained by the contact with the heat reservoir.

Two approaches are common to the simulation in canonical ensembles, – one is the feedback mechanism and other is suitable constraints that fix some or other parameter [30]. But no “direct” methods are known for the simulation of isobaric and adiabatic processes. In the latter case the correlated changes of temperature and volume should be obeyed to maintain the condition $dQ = 0$. Below we derive expressions for adiabatic and isobaric processes suitable for MD-simulations applicable to any systems. One dimensional lattice with N particles is considered here as an example.

3.1 Adiabatic process

Temperature T and lattice length L are conjugated variables in adiabatic process. Their changes dL and dT are related in such a way that the heat exchange with the heat bath $dQ = 0$. In other words small changes of both quantities in the phase plane (T, L) do not change the value of entropy $S(T, L)$: $dS = (\partial S/\partial L)dL + (\partial S/\partial T)dT = 0$. It means that the changes of temperature T and length L obey the relation

$$\frac{dT}{dL} = -\frac{\partial S/\partial L}{\partial S/\partial T}. \quad (19)$$

If the r.h.s. of (19) (as the function of T and L) is known at any point in the phase plane (T, L) then it is the ordinary differential equation for the adiabatic process $T(L)$. Thus the problem is to find partial derivatives of entropy $\partial S/\partial L$ and $\partial S/\partial T$ in adiabatic process.

The partial derivative $\partial S/\partial T = C_L/T$, where C_L is the heat capacity at constant length L . The heat capacity C_L is expressed through the variance σ_U of the total energy: $C_L = \sigma_U/T^2$ and σ_U is the sum of variances of kinetic and potential energies $\sigma_U = \sigma_{U_k} + \sigma_{U_p}$ as they are independent in canonical ensemble. But in canonical ensemble $\sigma_{U_k} = NT^2/2$, and assembling together all terms, one gets

$$\frac{\partial S}{\partial T} = \frac{N}{2T} + \frac{\sigma_{U_p}}{T^3}, \quad (20)$$

where $\sigma_{U_p} = \langle U_p^2 \rangle - \langle U_p \rangle^2$. This expression can be easily calculated in MD-simulation. There exists an analytical representation for $\langle U_p^2 \rangle$ in the case of exponential potential:

$$\langle U_p^2 \rangle = (N+1)T^2 [\mathcal{Z}_1 + (N+1)\mathcal{Z}_2]/\mathcal{Z}_0. \quad (21)$$

where integrals \mathcal{Z}_i are defined by (9).

Partial derivatives $\partial S/\partial L$ can be expressed through the force-energy correlator

$$\frac{\partial S}{\partial L} = \frac{1}{T^2} (\langle F_{N+1} U_p \rangle - \langle F \rangle \langle U_p \rangle). \quad (22)$$

Forces F between all neighboring particles are equal in the average and the mean value of all internal forces can be used for the better statistics. The fact that any of F_i can be used in (22) can be shown. But we start from the formal proving of the obvious fact that ensemble average of all forces are equal, i.e. $\langle F_1 \rangle = \langle F_2 \rangle = \dots \langle F_N \rangle$.

Let we have the definition of the ensemble average for F_{i+1} : $\langle F_{i+1} \rangle = Z_x^{-1} \int u'_{x_{i+1}}(x_{i+1} - x_i) \exp(-\beta U_p) d\Gamma$ (the derivative is taken with respect to x_{i+1}). First we note that $u'_{x_{i+1}}(x_{i+1} - x_i) = -u'_{x_i}(x_{i+1} - x_i)$, i.e. force acting on $(i+1)$ th particle from the left is equal to the force acting on i th particle from the right. Next for clarity we directly extract terms in $\langle F_{i+1} \rangle$ containing x_i and all other terms are denoted by Q . Then $\langle F_{i+1} \rangle = -Q \int u'(x_{i+1} - x_i) e^{-\beta u(x_i - x_{i-1})} e^{-\beta u(x_{i+1} - x_i)} dx_i = \frac{Q}{\beta} \int e^{-\beta u(x_i - x_{i-1})} [e^{-\beta u(x_{i+1} - x_i)}]' dx_i$ and integration by parts gives $Q \int u'_{x_i}(x_i - x_{i-1}) e^{-\beta u(x_i - x_{i-1})} e^{-\beta u(x_{i+1} - x_i)} dx_i = \langle F_i \rangle$. Thus the statement that $\langle F_{i+1} \rangle = \langle F_i \rangle$ is proven (every integration by parts shifts index ‘ i ’ to ‘ $i-1$ ’).

Analogous statement that $\langle F_{i+1} U_p \rangle = \langle F_i U_p \rangle$ is also easily demonstrated: $\langle F_{i+1} U_p \rangle = Z_x^{-1} \int u'(x_{i+1} - x_i) U_p \exp(-\beta U_p) d\Gamma = -Z_x^{-1} \frac{\partial}{\partial \beta} \int u'(x_{i+1} - x_i) \exp(-\beta U_p) d\Gamma$ and integration by parts, as described above, gives the identity $\langle F_{i+1} U_p \rangle = \langle F_i U_p \rangle$.

Taking into account (20) and (22) the final expression for the adiabatic process has the form:

$$\frac{dT}{dL} = -\frac{\langle F_i U_p \rangle - \langle F \rangle \langle U_p \rangle}{NT/2 + \sigma_{U_p}/T}. \quad (23)$$

Technically, it is necessary to calculate the following mean values: $\langle U_p \rangle$, $\langle U_p^2 \rangle$, $\langle F \rangle$ and $\langle F_i U_p \rangle$ at any point of the phase plane (T, L). The technique of MD-simulation is discussed below.

The expression (23) for the adiabatic process is valid for any type of potential but it can be simplified for the exponential potential. The reason is the equation of state (13) which relates $\langle U_p \rangle$ and $\langle F \rangle$. Moreover, the force F_i in the correlator $\langle F_i U_p \rangle$ also can be substituted by $U_p/(N+1)$, and the numerator in (23) is $\sigma_{U_p}/(N+1)$. Then the final expression (23) for the adiabatic process for the exponential potential is:

$$\frac{dT}{dL} = -\frac{\sigma_{U_p}}{(N+1)(NT/2 + \sigma_{U_p}/T)}. \quad (24)$$

It is convenient to express (24) through the dimensionless deformation $\varepsilon = L/(N+1)$. Then (24) is simplified to

$$\frac{dT}{d\varepsilon} = -\frac{\sigma_{U_p}}{NT/2 + \sigma_{U_p}/T} \quad (25)$$

and the derivative $dT/d\varepsilon$ depends only on one variable – the variance σ_{U_p} of the potential energy. Expression (25)

is further employed in MD-simulation for the exponential potential, and it allows to estimate the accuracy and reliability of the suggested approach. It is important to note that the calculations of all necessary mean values are performed in the equilibrium state of the system.

3.2 Isobaric process

Now we get the formulae for the isobaric process and again consider the 1D lattice of particles with nearest-neighbor interaction at arbitrary deformation L (in 1D case the isobaric process is process at constant force $\langle F \rangle$). The conjugated thermodynamical variables for the isobaric process are also temperature T and length L . But it is convenient to use other pair of variables: $\beta = 1/T$ and L . The isobaric ($d\langle F \rangle = 0$) equation is

$$\frac{d\beta}{dL} = -\frac{\partial\langle F \rangle/\partial L}{\partial\langle F \rangle/\partial\beta}, \quad (26)$$

where $\langle F \rangle = \frac{1}{\beta Z_x} \frac{\partial Z_x}{\partial L}$ is the force acting on the right lattice end. Expression (26) again is the ordinary differential equation and the partial derivatives in (26) should be expressed through the values which can be found in MD-simulation.

The partial derivative $\partial\langle F \rangle/\partial L$ can be rewritten as

$$\frac{\partial\langle F \rangle}{\partial L} = \frac{\partial}{\partial L} \left(\frac{1}{\beta Z_x} \frac{\partial Z_x}{\partial L} \right) = -\beta\langle F \rangle^2 + \frac{1}{\beta Z_x} \frac{\partial^2 Z_x}{\partial L^2}. \quad (27)$$

First derivative $\frac{\partial Z_x}{\partial L} = -\beta \int d\Gamma_x \exp(-\beta U_p) u'(L - x_N)$. But $-u'(L - x_N) = -u'(x_{N+1} - x_N)$ is nothing else then the force acting on the right lattice end, then

$$\frac{\partial Z_x}{\partial L} = \beta \int d\Gamma_x \exp(-\beta U_p) F_{N+1}. \quad (28)$$

Again, as stated above, equation (28) can be integrated by parts several times and every integration diminishes the index at F by unity. After $(N - i)$ integrations of (28) by parts one can get

$$\frac{\partial Z_x}{\partial L} = \beta \int d\Gamma_x \exp(-\beta U_p) F_i, \quad (i = 1, 2, \dots, N). \quad (29)$$

The second differentiation in (27) by L and $(N - j)$ times integration by parts gives

$$\frac{\partial^2 Z_x}{\partial L^2} = \beta^2 \int d\Gamma_x \exp(-\beta U_p) F_i F_j. \quad (30)$$

Using the definition of thermodynamic mean values one gets

$$\frac{1}{Z_x} \frac{\partial^2 Z_x}{\partial L^2} = \langle F_i F_j \rangle \quad (31)$$

and

$$\frac{\partial F}{\partial L} = \beta (\langle F_i F_j \rangle - \langle F \rangle^2). \quad (32)$$

The independence of the force-force correlator $\langle F_i F_j \rangle$ value on the distance $|j - i|$ (the long-range correlation order) seems very strange. All other correlators behave normally, e.g. interparticle energy-energy correlator $\langle u(y_i) u(y_j) \rangle$ tends to the product of mean values $\langle u(y_i) \rangle \langle u(y_j) \rangle$ at $|j - i| \rightarrow \infty$ as it should be.

The partial derivative $\partial\langle F \rangle/\partial\beta$ can be expressed as

$$\frac{\partial\langle F \rangle}{\partial\beta} = -\frac{1}{\beta^2} \frac{1}{Z_x} \frac{\partial Z_x}{\partial L} - \frac{1}{\beta Z_x^2} \frac{\partial Z_x}{\partial\beta} \frac{\partial Z_x}{\partial L} + \frac{1}{\beta Z_x} \frac{\partial^2 Z_x}{\partial\beta \partial L}. \quad (33)$$

But $\frac{1}{\beta Z_x} \frac{\partial Z_x}{\partial L} = \langle F \rangle$ and $\frac{1}{Z_x} \frac{\partial Z_x}{\partial\beta} = -\langle U_p \rangle$, then

$$\frac{\partial\langle F \rangle}{\partial\beta} = -\frac{\langle F \rangle}{\beta} + \langle U_p \rangle \langle F \rangle + \frac{\partial^2 Z_x}{\partial\beta \partial L}. \quad (34)$$

As it follows from (29), $\partial Z_x/\partial L = \beta \int d\Gamma_x \exp(-\beta U_p) F_i$, therefore

$$\frac{\partial^2 Z_x}{\partial\beta \partial L} = -\beta \int d\Gamma_x \exp(-\beta U_p) F_i U_p + \int d\Gamma_x \exp(-\beta U_p) F_i \quad (35)$$

and

$$\frac{1}{\beta Z_x} \frac{\partial^2 Z_x}{\partial\beta \partial L} = -\langle F_i F_j \rangle + \langle F \rangle/\beta. \quad (36)$$

The expression for the partial derivative $\partial F/\partial\beta$ is

$$\frac{\partial\langle F \rangle}{\partial\beta} = \langle U_p \rangle \langle F \rangle - \langle F_i F_j \rangle. \quad (37)$$

The final expression for the isobaric process in variables (β, L) is:

$$\frac{d\beta}{dL} = -\frac{\partial\langle F \rangle/\partial L}{\partial\langle F \rangle/\partial\beta} = \beta \frac{\langle F \rangle^2 - \langle F_i F_j \rangle}{\langle U_p \rangle \langle F \rangle - \langle U_p F_i \rangle} \quad (38)$$

or in standard variables (T, L) ,

$$\frac{dT}{dL} = T \frac{\langle F_i F_j \rangle - \langle F \rangle^2}{\langle U_p \rangle \langle F \rangle - \langle U_p F_i \rangle}. \quad (39)$$

Expression (39) for the isobaric process is further simplified for the exponential potential:

$$\frac{dT}{d\varepsilon} = \frac{T\langle U_p \rangle - \sigma_{U_p}}{\sigma_{U_p}/T}, \quad (\varepsilon = L/(N + 1)). \quad (40)$$

4 MD-simulation of thermodynamic processes

MD-simulation is the most convenient method to calculate necessary mean values entering in the r.h.s. of equations for the adiabatic and isobaric processes, i.e. (23) and (39), correspondingly. MD-simulation in canonical ensemble is equivalent to the solution of stochastic differential equations

$$\frac{d^2 x_i}{dt^2} = -\frac{\partial U_p}{\partial x_i} + \mathcal{F}_i; \quad i = 1, 2, \dots, N, \quad (41)$$

where x_i – displacement of i th particle from equilibrium; $U_p = \sum_{i=1}^{N+1} u(x_i - x_{i-1})$ is the sum of $(N + 1)$ bonds energies between neighboring particles in the lattice with rigid boundaries.

The thermal contact with the heat bath is simulated by Langevin forces $\mathcal{F}_i = \xi_i - \gamma \dot{x}_i$ acting on every particle. Random values ξ_i with spectral properties $\langle \xi_i \rangle = 0$ and $\langle \xi_i(t_1) \xi_j(t_2) \rangle = 2\gamma T \delta_{ij} \delta(t_1 - t_2)$ provide temperature T ; the viscous friction coefficient is chosen $\gamma = 1$ for definiteness; this value defines only the dynamics (the less γ value, the more “inertial” is system). And we note that in thermodynamic equilibrium the thermodynamic functions do not depend on γ . If the heat bath is modelled by the Langevin forces then from the Fokker–Planck equation it follows that the equilibrium state corresponds to the Gibbs ensemble. An alternative approach suggested by Nosé and Hoover [31,32] was motivated by the need to overcome the difficulties of dealing with stochastic processes. The comprehensive analysis of both Langevin and Nosé–Hoover methods and their comparison is presented in review [33].

Stochastic differential equations (41) are solved by the fourth order Runge-Kutta method. Random values $\{\xi\}$ are related to the integration step h and are chosen from the uniform random distribution on the interval $[-\sqrt{6\gamma T/h}, \sqrt{6\gamma T/h}]$ if temperature T and friction parameter γ are specified.

As stated above, all mean values in the r.h.s. of equations (23) and (39) for adiabatic and isobaric processes, correspondingly, should be calculated in the equilibrium state. Thus, the system must achieve the thermodynamic equilibrium starting from an arbitrary initial state (see Appendix (5) on the thermalization kinetics). Initial conditions are usually chosen in the form $\mathbf{x} = 0$, $\mathbf{v} = 0$, i.e. all particles are at rest and at equilibrium.

There are different methods to calculate mean values in MD-simulation [30]. The most efficient method to calculate mean values and their standard errors is the following. After the system achieves its equilibrium, the MD-trajectory is separated into M rather long parts. Every fraction of trajectory has equal temporary length $\Delta t = t_j - t_{j-1}$ ($j = 1, 2, \dots, M$). If mean values $\langle U_p \rangle$, $\langle U_p^2 \rangle$, $\langle F \rangle$, $\langle U_p F_i \rangle$, $\langle F_i F_j \rangle$ should be calculated, then the following ordinary differential equations

$$\begin{aligned} \dot{y}_1 &= U_p(t), \quad \dot{y}_2 = U_p^2(t), \quad \dot{y}_3 = F_i(t), \\ \dot{y}_4 &= U_p(t)F_i(t), \quad \dot{y}_5 = F_i(t)F_j(t) \end{aligned} \quad (42)$$

are added to the system of equations (41) and they are solved jointly. The r.h.s. of equations (42) are easily calculated by MD method. The corresponding value of, e.g. $\langle U_p \rangle^j$, on j th time interval is calculated as

$$\langle U_p \rangle^j = (\Delta t)^{-1} \int_{t_{j-1}}^{t_j} \dot{y}_1(t) dt \quad (43)$$

and the total mean value is calculated as $\langle U_p \rangle = M^{-1} \sum_{j=1}^M \langle U_p \rangle^j$. This approach essentially speeds up the convergence and accuracy.

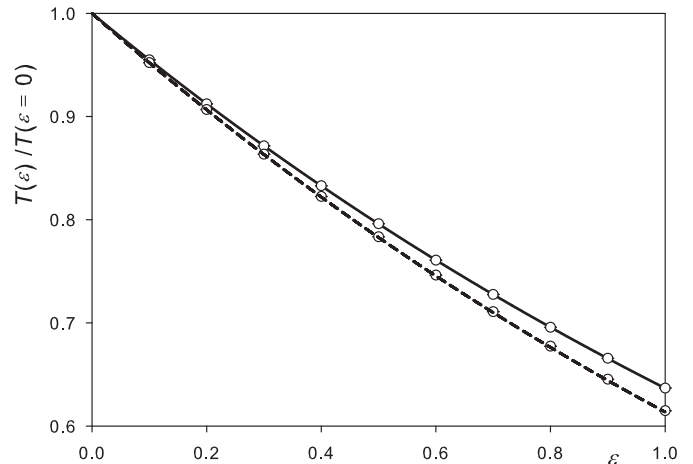


Fig. 1. Adiabats (relations of temperatures in the process and before elongation) vs. elongation ε for two values of initial temperatures. Upper curve: $T(\varepsilon = 0) = 1.0$, lower curve: $T(\varepsilon = 0) = 0.2$. Circles: results of MD-simulation; solid and dashed lines: analytical results. Standard errors are less than the symbol sizes and are maximal at $\varepsilon = 1.0$ ($\approx 0.2\%$). $N = 10$, $M = 10^5$, $\gamma = 1$.

The knowledge of necessary mean values calculated in the equilibrium state at some points of the phase planes (T, L) for adiabatic and isobaric processes, determine the corresponding gradients $\nabla S = 0$ or $\nabla P = 0$. It allows to go to the new point in the phase plane ($T' = T + dT$, $L' = L + dL$) moving along adiabats or isobars thus fully describing the corresponding thermodynamic process.

4.1 Adiabatic “temperature-deformation” in canonical ensemble

The advanced method is illustrated as an example for the adiabatic process for the N -particles lattice with the exponential potential. The method is appropriate for an arbitrary number of particles ($N = 2, 3, \dots, \infty$) and $N = 10$ is chosen for the definiteness. The adiabats are calculated by two methods: first – MD-simulation using the numerical integration of differential equation (25), and the second – the analytical approach as the numerical solution of equation (11) at $S = \text{const}$. Here for the chosen values of ε the corresponding values of T were calculated numerically. These two methods allow to compare the reliability and accuracy of MD-simulation.

Adiabats for two different initial temperatures are shown in Figure 1. The ordinary differential equation (25) was solved numerically for $T = T(\varepsilon)$ (the Runge-Kutta method, integration step $h = 0.1$; $M = 10^5$). One can see $\sim 35\%$ temperature decrease under 100% elongation. Very good agreement ($\delta T(\varepsilon) \approx 0.2\%$) between analytical and MD results is obtained.

Few words about the adiabatic process at low temperatures should be said. Earlier it was shown [27] that the corresponding equation in microcanonical ensemble has the form $T(\varepsilon) \sim \sqrt{u''(\varepsilon)}$, where u is the interparticle

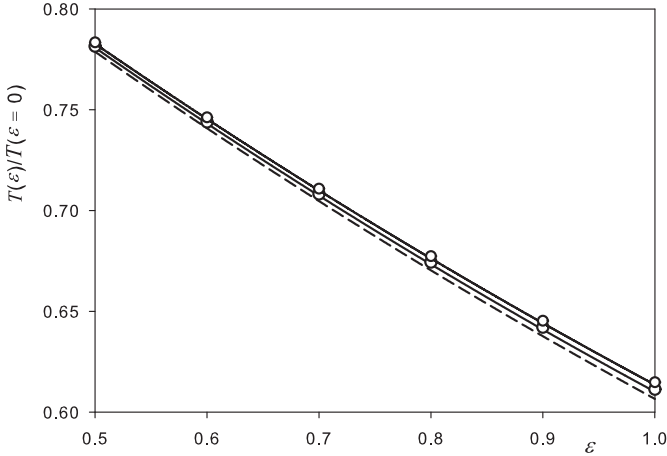


Fig. 2. Adiabats at low initial temperatures $T(\varepsilon = 0) = 0.1$ and $T(\varepsilon = 0) = 0.2$ in the range of elongation $0.5 \leq \varepsilon \leq 1.0$. Upper curve: $T(0) = 0.2$, lower curve: $T(0) = 0.1$. Circles: MD-simulation; solid lines: analytical results; dashed line: dependence $T \propto \exp(-\varepsilon/2)$ in the quasi-harmonic limit. $N = 10$, $M = 10^5$, $\gamma = 1$.

potential at specific elongation ε . This relation is also valid in the canonical ensemble. To show this we calculate the entropy S of the harmonic lattice with the rigidity constant $g = \sqrt{u}$. Then $S = (N/2) \ln(T^2/g)$, and the adiabat equation $S = \text{const.}$ gives $T^2 \propto g$. But under the quasi-harmonic lattice elongation (at low temperatures) the potential energy expansion near the equilibrium gives $g \propto u(\varepsilon)$. Thus we have the same equation for the adiabatic process as in the microcanonical ensemble: $T \sim \sqrt{u(\varepsilon)} = \exp(-\varepsilon/2)$. Adiabats at low temperatures ($T = 0.1$ and $T = 0.2$) are shown in Figure 2.

The suggested method was also checked for the lattice with Morse potential and good agreement (accuracy $\lesssim 0.2\%$) was also obtained.

It should be noted that the r.h.s. of expressions (23) and (39) for the adiabatic and isobaric processes has no limitations on the dimensionality (1D, 2D, or 3D) and interaction potentials, and these equations define corresponding processes for *arbitrary* systems.

5 Conclusion

New method is developed which allows to model any quasi-stationary processes by MD-simulation in canonical ensemble for arbitrary potentials of interaction and arbitrary systems (dense gas, condensed state and others). Though the partition function and entropy can not be calculated directly by this MD method, expressions which allow to calculate the partial derivatives of entropy and pressure, which enter into the expressions for adiabatic and isobaric processes are obtained. These equations enable to calculate thermodynamic processes in arbitrary classical systems.

Analytical expressions for thermodynamic variables (partition function, entropy and others) are also derived

for 1D systems with arbitrary potentials of interactions of neighboring particles. It was done due to function (2), which actually is the analytical continuation of the Fourier transformation to the complex plane. Necessary integrals are evaluated numerically.

The suggested method of the MD-simulation of thermodynamic processes is verified for the exponential repulsive and Morse potentials. Analytical results for this potential allow to compare them with results of numerical simulation. The coincidence is very good what corroborates the reliability and accuracy of the suggested approach.

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Appendix A: Thermodynamics of the 1D lattice with exponential potential in (F, T) ensemble

Below we get the thermodynamic expressions for the exponential potential in the thermodynamic limit and compare them with corresponding expressions obtained by Toda [13]. To make the transformation from variables (L, T) to (F, T) ones, it is necessary to change the last term $\exp[-(L - x_N)]$ in the expression for the potential energy (8) to the term with force, i.e. to the product Fx_N (here and below the notation $F = \langle F \rangle$ is used for clarity). Then the partition function is

$$Z = \left[\frac{\Gamma(\beta F)}{\beta \beta F} \right]^N \quad (\text{A.1})$$

and an expression for the mean lattice length L in variables (F, T) is valid:

$$L \equiv \langle x_N \rangle = -\frac{1}{\beta} \frac{\partial Z}{\partial F} = N [\ln \beta - \Psi(\beta F)], \quad (\text{A.2})$$

where $\Psi(\dots)$ – logarithmic derivative of the Gamma-function.

The evaluation of the partition function should be performed by the saddle-point method, and the saddle-point x_0 for the integration along the line $\text{Re } z = x_0$ can be found from an equation

$$\Psi(x_0) + \ln \left[\frac{\exp(\varepsilon)}{\beta} \right] = 0 \quad (\text{A.3})$$

with solution

$$\varepsilon = \ln \beta - \Psi(x_0). \quad (\text{A.4})$$

Our answer for the lattice expansion (A.4) can be compared with the result of Toda. To do it the value x_0 should be evaluated. An expression for F , which is the relation of two integrals (12)

$$F = \frac{1}{\beta} \frac{Z_1}{Z_0} \quad (\text{A.5})$$

in the thermodynamical limit is equal to $Z_1/Z_0 = x_0$. Then $x_0 = \beta F$ and expression (A.4) coincides with Toda's (M. Toda define this value as "thermal expansion" \bar{r}).

The Toda's answer for the mean value of the potential energy at first glance differs from ours. The reason is that Toda defines this value as

$$U_p^{(T)} = \frac{\partial \ln Z_T}{\partial \beta} = N [F \ln \beta + F - F \Psi(\beta F)] \quad (\text{A.6})$$

and the energy of the 'external field' $F\langle x_N \rangle$ is included in (A.6). But if the potential energy is defined as the difference of total energy and the energy of deformation $F\langle x_N \rangle$ (an expression for $\langle x_N \rangle$ see above, (A.2)), then

$$U_p^{(T)} - F\langle x_N \rangle = NF, \quad (\text{A.7})$$

what in the thermodynamical limit coincides with our result (13).

Appendix B: Relaxation of different values to stationary states: thermalization

The MD-simulation starts from an arbitrary initial state and some time is necessary to reach the equilibrium in the canonical ensemble. In this section we briefly analyze the relaxation rates of different values (kinetic and potential energies, vibrational modes, velocity distribution functions) to their stationary states. The lattice of $N = 10$ particles with the exponential potential is considered as an example; viscous friction coefficient in Langevin forces $\gamma = 1$.

B.1 Relaxation of kinetic and potential energies to equilibrium

The relaxations of the kinetic and potential energies to their equilibrium states are shown in Figure 3. Initially all particles are at rest ($v_i = 0$) and at equilibrium positions for the chosen elongation ε : $x_i = i\varepsilon$, ($i = 1, 2, \dots, N$). The equilibrium value of the specific kinetic energy at $T = 1$ in canonical ensemble is $\langle U_k \rangle / N \equiv T/2 = 0.5$. The equilibrium value of the specific potential energy is less because of the non-linearity and calculated according to (10) is $\langle U_p \rangle / N = 0.4606$.

The kinetic energy relaxes to the equilibrium value $\langle U_k \rangle / N = 0.5$ rather fast. The relaxation law is exponential: $T/2 - [\langle U_k \rangle(t)] / N \propto \exp(-t/\tau)$, where $\tau \simeq 1.23$. The specific kinetic energy relaxes to the equilibrium with the same rate for different number of particles (see inset to Fig. 3).

Surprisingly the potential energy relaxes slower. It was expected that the Langevin sources should ensure equal relaxation rates for both kinetic and potential energies. The relaxation rate for potential energy is power-like: $[\langle U_p(t = \infty) \rangle - \langle U_p(t) \rangle] / N \propto t^{-\nu}$. And in contrast to the kinetic energy, the exponent ν depends on the number of particles: $\nu \simeq 1.6$ for $N = 10$, $\nu \simeq 0.72$ ($N = 50$)

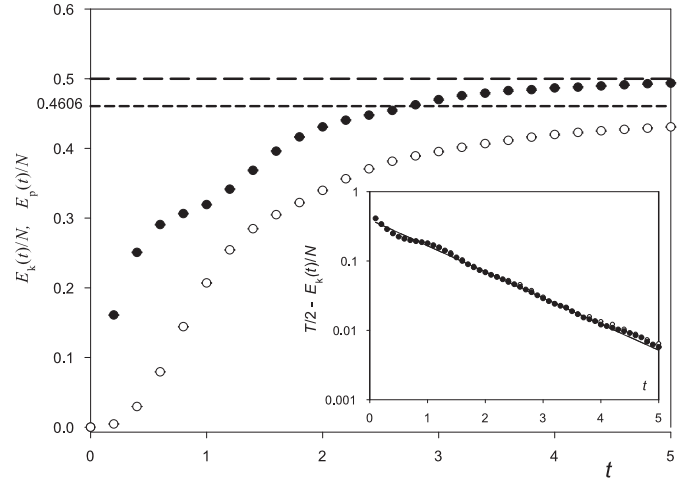


Fig. 3. Relaxation of the specific kinetic (filled circles) and potential (empty circles) energies to their equilibrium values. Upper dashed line: $E_k/N = 0.5$, lower: $E_p/N = 0.4606$. Standard errors are less than the symbol sizes. In inset: relaxation of the kinetic energy in log-linear coordinates for two lengths of lattice: $N = 10$ (filled circles) and $N = 100$ (empty circles). Solid line: fitting $T/2 - E_k(t)/N = a \exp(-t/\tau)$ and $\tau \simeq 1.23$. $N = 10$, $T = 1$, $\varepsilon = 0$, $\gamma = 1$, $M = 2 \times 10^4$.

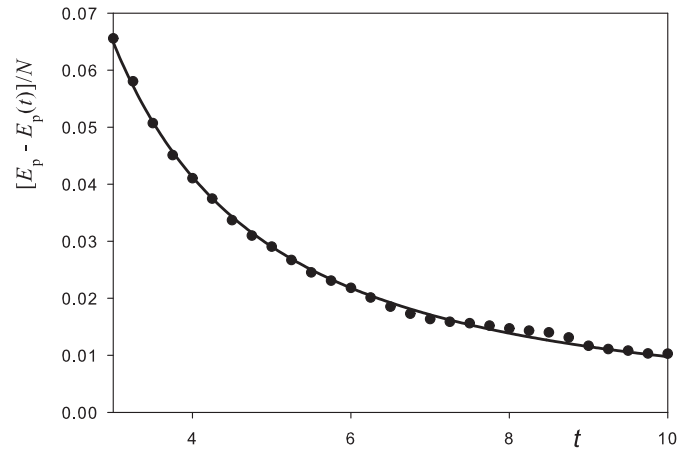


Fig. 4. Power law fitting of the potential energy relaxation rate. Circles: MD-simulation, solid line: power law $[E_p(t = \infty) - E_p(t)] / N = 0.365/t^{1.57}$. $N = 10$, $T = 1$, $\varepsilon = 0$, $\gamma = 1$, $M = 10^5$.

and $\nu \simeq 0.65$ ($N = 100$), i.e. the relaxation time of the potential energy increases with the growth of N . Figure 4 illustrates the power law of the potential energy relaxation. Below, we show that this fact is determined by the relaxation of the long-wave vibrational modes.

B.2 Relaxation to equilibrium of the one-particle velocity distribution function

The fulfillment of the Maxwell velocity distribution is often supposed to be the sufficient condition of achievement

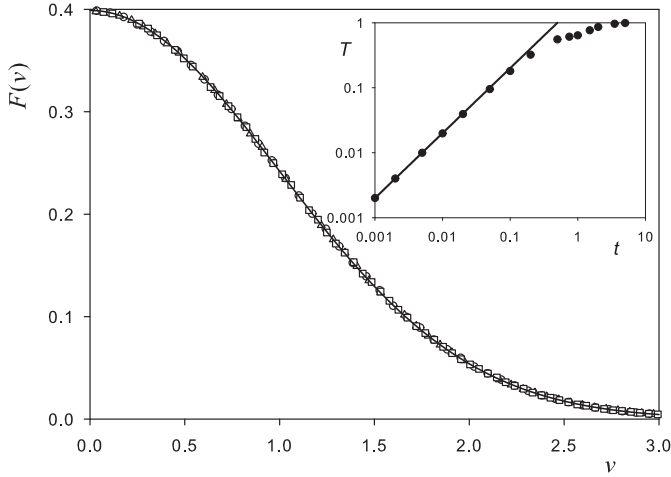


Fig. 5. Scaled distribution functions at different times: $t = 0.01$ (diamonds), $t = 0.1$ (triangles), and $t = 1.0$ (squares). Calculated values ideally match the Maxwell distribution function at all times (solid line). Instantaneous temperatures are: $T(t = 0.01) = 0.0198$, $T(t = 0.1) = 0.1800$, $T(t = 1.0) = 0.6386$. In inset: the dependence of temperature vs. time in log-log coordinates. $N = 10$, $\varepsilon = 0$, $\gamma = 1$, $M = 10^5$.

of thermodynamic equilibrium [30]. But we show that this is not always the case.

The initial conditions are chosen in the form $(\mathbf{x}, \mathbf{v}; t = 0) = \delta(\mathbf{x})\delta(\mathbf{v})$, i.e. all particles are at rest and at their equilibrium positions. And the lattice is heated from the initial state at $T = 0$ up to the temperature $T = 1$ determined by the Langevin sources.

There are two regimes in heating. The first one – at small times when the lattice can be considered as quasi-harmonic (small velocities and relative displacements at low energies mean weak inharmonism). It can be demonstrated that the Maxwell distribution is the inherent property of the harmonic lattice in the canonical ensemble. The second regime is realized for larger times, when the non-linearity becomes essential. Then the system reaches Gibbs equilibrium and the one-particle velocity distribution function is again of Maxwell type.

Figure 5 illustrates the velocity distribution function at three times: $t_1 = 0.01$, $t_2 = 0.1$ and $t_3 = 1.0$ with correspondingly increasing temperatures $T(t_1) = 0.0198$, $T(t_2) = 0.1800$ and $T(t_3) = 0.6386$. The distribution functions, having different temperatures T_k at different times t , are brought to $T = 1$ by scaling of distribution functions $F \rightarrow F T_k^{1/2}$ and velocities $v \rightarrow v T_k^{-1/2}$.

The dependence of temperature vs. time is shown in the inset to Figure 5 and it is well approximated by $T(t) \sim [1 - \exp(-2t)]$. At small time the linear dependence $T \propto 2t$ is observed. The deviation from the Maxwell distribution is not detected even at very small times $\lesssim 10^{-5}$ (few very small integration steps). It means that the achievement of the Maxwell velocity distribution is practically instantaneous. The rate of achieving the equilibrium Maxwell distribution doesn't depend on the lattice length N .

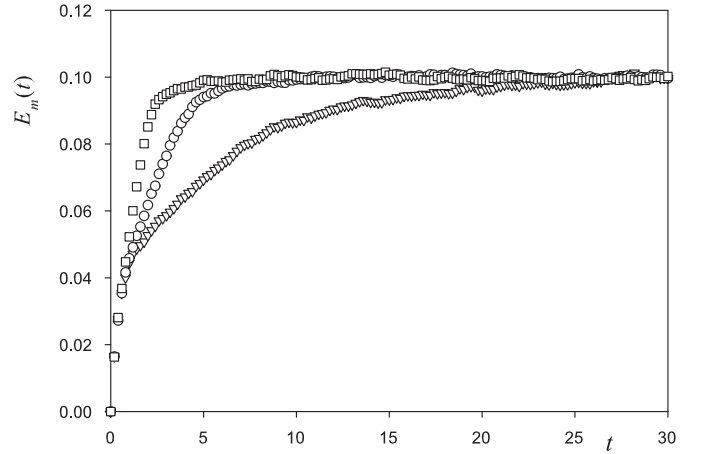


Fig. 6. Energy relaxation of three vibrational modes (the longest-wave E_1 (squares), the second E_2 (circles) and the fifth E_5 (triangles down) modes) to their equilibrium value $\simeq T/N = 0.1$. $N = 10$, $T = 0.1$, $\varepsilon = 0$, $\gamma = 1$, $M = 10^4$.

B.3 Relaxation of vibrational modes to equilibrium

The normal vibrational modes \mathcal{E}_m ($m = 1, 2, \dots, N$) are well defined only at comparatively low energies (temperatures). That is why the temperature $T = 0.1$ was chosen for the analysis of the vibrational modes relaxation rates. The relaxation of few vibrational modes \mathcal{E}_m ($m = 1, 2, 5$) to their equilibrium states is shown as an example in Figure 6. One can see that the longest-wave vibration has the slowest relaxation rate. Namely, the behavior of this mode determines the overall relaxation rate to equilibrium.

Our findings differ from results of A. Bikaki et al. [34] on the energy relaxation in nonlinear lattices in one and two spatial dimensions where hierarchies of discrete breathers (DBs) that relax with different time constants were found. In our numerical simulation in canonical ensemble no contribution of DBs was detected in heating from $T = 0$ up to as high temperature as $T = 1$.

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