

Translation of the original article

Vinogradov G.A., Lakhno V.D. *Mathematical Biology and Bioinformatics*. 2025;20(1):31–46.

doi: [10.17537/2025.20.31](https://doi.org/10.17537/2025.20.31)

===== TRANSLATIONS OF PUBLISHED ARTICLES =====

On the Thermalization of One-Dimensional Lattices. II. Canonical Ensemble

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Abstract. In this paper, thermalization of one-dimensional lattices in a canonical ensemble is considered. The main thermalization methods are described, including the Nosé–Hoover algorithm and the stochastic Langevin method. Thermalization of lattices with a “rigid” symmetric β -Fermi-Pasta-Ulam-Tsingou (β -FPUT) potential is considered in detail. This example demonstrates quantitative and qualitative characteristics of the thermalization process. In the next section, thermalization of a lattice with a “soft” asymmetric Peyrard-Bishop-Holstein (PBH) potential is analyzed. Thermalization of this lattice has some peculiarities associated with the type of the Morse potential, which models hydrogen bonds between DNA strands. In conclusion, the problem of quantum thermalization is mentioned, when the quantum nature of the vibrational motion of the atoms of a molecular chain is taken into account.

Key words: *canonical ensemble, thermalization, Langevin thermostat*

INTRODUCTION

There are two variants of statistical ensembles. A microcanonical ensemble is an isolated system with a constant energy value. If the ergodic hypothesis is true, then all microscopic states in this ensemble are equally probable. Thermalization in a microcanonical ensemble has been studied in detail. Various thermalization scenarios have been considered and the results of the analysis have contributed to the emergence of new ideas and research directions in statistical physics. The previous work [1] was devoted to the consideration of thermalization in a microcanonical ensemble.

A canonical ensemble is used to model real physical processes, since it allows one to describe the interaction of the system with the environment and to record the temperature. In this case, the physical system exchanges energy with the environment (thermostat), being in thermal equilibrium with it.

In any thermalization method, there are always parameters that determine the time required to reach a steady-state temperature value and energy fluctuations due to the action of external factors. In the case of large fluctuations, the system dynamics ceases to be Newtonian and, in the limiting case, can acquire a Brownian character. Therefore, the question arises as

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to what extent these fluctuations affect the dynamics of the process under study and, ultimately, influence the results obtained. Another difference between thermalization in the microcanonical and canonical ensembles is the “internal” time of numerical modeling, which determines, among other things, the integration step. If the microcanonical ensemble provides a natural characteristic time determined only by the parameters of the original model, then, for example, in Langevin dynamics an additional time scale arises, specified by an arbitrary value of the attenuation parameter. It is only in the specialized literature devoted to the methodology of molecular modeling (MD) that information can be found on the optimal choice of thermalization parameters. Therefore, thermalization in the canonical ensemble is considered in this paper in more detail and is accompanied by some examples.

The first section describes the most well-known thermalization methods in the canonical ensemble. In the second section, the thermalization of the β -FPUT lattice with the interaction potential of neighboring particles $U(y) = \frac{1}{2}y^2 + \frac{\beta}{4}y^4$ is considered. The Langevin thermostat is used to thermalize the system. The influence of the thermostat parameters on the characteristics of the stationary state of the system is considered. In addition to the necessary quantitative characteristics (time to reach a steady-state temperature, fluctuation variance), some qualitative properties of the thermalized system (phase portrait, “entropy” of average values) are also given. The next section is devoted to the thermalization of the system in the Peyrard-Bishop-Holstein (PBH) model. The last section briefly discusses quantum thermalization.

THERMOSTATS FOR THERMALIZATION OF LATTICES

The idea to use molecular dynamics (MD) for simulations of lattices in a canonical ensemble is to fix the temperature T . For systems with one degree of freedom, the temperature of the system is related to the average kinetic energy of the particle by the ratio $\langle E_{\text{kin}} \rangle = \frac{1}{2}k_B T$. Although the average values of the kinetic energy and temperature are kept fixed, the instantaneous values of the kinetic energy fluctuate.

When calculations by the MD method are carried out in a canonical ensemble, then in the course of modeling certain processes, the question naturally arises of maintaining temperature constancy. There are several methods for adding and decreasing energy to a system in order to approximate the system with a canonical ensemble. The most popular temperature control methods include the Andersen thermostat, Berendsen thermostat, Nosé–Hoover thermostat, Langevin stochastic thermostat, and collision thermostat. And the purpose of any thermostat is to ensure (on average) the consistency of the required system temperature. These thermostats are briefly described below.

Andersen thermostat

When using the Andersen thermostat [2], two parameters are selected: T_0 and λ . T_0 is the desired temperature of the system. And λ is a parameter that determines the frequency of stochastic collisions. This parameter determines the intensity of the system's connection with the heat reservoir. If the sequence of collisions is uncorrelated, then the distribution of time intervals between two subsequent collisions $P(t; \lambda)$ is a continuous Poisson distribution:

$$P(t; \lambda) = \lambda e^{-\lambda t},$$

where $P(t; \lambda)dt$ is the probability that the next collision will occur in the time interval $[t; t + dt]$.

The simulation to achieve a constant required temperature T_0 is implemented as follows. At some time t , the system is characterized by two vectors of state $\mathbf{x}(t)$ and $\mathbf{v}(t)$. Then, the dynamics equations are integrated over the time interval until the next stochastic collision. A particle undergoing a collision is randomly selected. The velocity of this particle is randomly

selected from the Boltzmann distribution for this temperature. The velocities of the remaining particles do not change. After that, the dynamics equations are integrated again until the next stochastic collision, determined by the Poisson equation. And this process is repeated many times.

It has been proven that Andersen algorithm does generate a canonical distribution. In this case, the time average of some quantity calculated from the Andersen MD trajectory is equal to the value calculated from the canonical Gibbs ensemble. This is the advantage of Andersen thermostat.

However, Anderson thermostat has its drawbacks. First, it technically requires a very large number of collisions in order to reach equilibrium temperature. Second, the collisions randomly change the particle velocities. And this does not obey the laws of Newton dynamics. Therefore, the dynamics themselves become somewhat non-physical.

Berendsen thermostat

One of the main problems with thermalization methods that use velocity renormalization is that these methods do not allow for natural temperature fluctuations that are necessarily present in the canonical ensemble. To overcome this difficulty, Berendsen introduced a method of weak coupling with an external thermostat.

The Berendsen thermostat [3], also called a proportional thermostat, corrects deviations of the actual temperature T from the prescribed temperature T_0 by multiplying all velocities by a certain coefficient ξ , thereby “moving” the dynamics of the system towards the temperature T_0 .

In the Berendsen thermostat, the rates are renormalized at each integration step so that the rate of changes in the temperature is proportional to the temperature difference:

$$\frac{dT}{dt} = \frac{1}{\tau}(T_0 - T),$$

where τ is the coupling parameter that determines the rate of temperature change.

Thermalization is technically carried out by renormalizing the momenta at the k -th integration step $\mathbf{p}^k \rightarrow \xi \mathbf{p}^k$ using the transformation coefficient:

$$\xi^2 = 1 + \frac{\Delta t}{\tau_T} \left(\frac{T_0}{T} - 1 \right),$$

where Δt is the time interval after which the renormalization of velocities occurs, and τ_T is the characteristic time of establishing thermal equilibrium; Δt and τ_T are the parameters of the thermostat.

The Berendsen thermostat cannot generate the correct canonical ensemble, especially for small systems. It only provides an exponential approximation to the specified temperature. However, this thermostat, due to its speed and efficiency in temperature control, is sometimes used for large systems. And then the Berendsen thermostat can provide a fairly accurate description of the statistical properties. The shortcomings of the Berendsen thermostat can be corrected by using its modification [4].

Nose-Hoover thermostat

At a constant temperature, the energy of a system of N particles fluctuates. Therefore, in modeling it is necessary to use mechanisms that would provide the necessary fluctuations. A Hamiltonian was proposed that provides a deterministic, rather than stochastic, thermalization algorithm with time-reversible equations [5–7].

The heat reservoir in the Nose–Hoover (NH) thermostat consists of only one imaginary particle. However, when modeling systems, conditions of constant temperature are achieved,

and the statistics obey the Gibbs distribution.

The functional of the energy of the NH has the form:

$$H_{HX} = \sum_i \frac{p_i^2}{2m_i s^2} + \sum_{i,j} V(q_i, q_j) + \frac{p_s^2}{2Q} + Nk_B T \ln(s), \quad (1)$$

where the first two terms in H_{HX} are the kinetic and potential energies of the system. In addition to the N degrees of freedom, one more artificial degree of freedom s is added. The third term in (1) is the kinetic energy of the particle s and Q is a parameter having the dimension of mass. This parameter is carefully selected. The last term is the thermal energy of the system adjusted by the factor $\ln(s)$. The indices i and s refer to the lattice particles and the fictitious particle s , respectively.

To solve the equations that follow from (1), we need to turn to renormalized coordinates. Renormalization is carried out as follows:

$$\mathbf{q}' = \mathbf{q}, \mathbf{p}' = \mathbf{p}/s, dt' = dt/s,$$

and $\mathbf{q}(t)$ and $\mathbf{p}(t)$ are the vectors of the system state. Then the equations of motion for the renormalized coordinates and momenta have the form:

$$\frac{dq_i}{dt} = \frac{p_i}{m_i s^2}, \frac{dp_i}{dt} = -\frac{\partial V(q_i, q_j)}{\partial q_i},$$

and the equations for the particle s

$$\frac{ds}{dt} = \frac{p_s}{Q}, \frac{dp_s}{dt} = \frac{1}{s} \left(\sum_i \frac{p_i^2}{m_i s^2} - Nk_B T \right).$$

If the initial conditions in the simulation start from zero velocities, then some problems arise related to the fact that the lattice particles acquire energy with large decelerations. This can cause the system temperature to exceed the prescribed temperature and may even begin to oscillate. An acceptable way to solve this problem is to make the initial conditions somewhat chaotic. Some disadvantage of the NH thermostat is the non-ergodicity of small systems and the system of harmonic oscillators. This defect is eliminated by the Nosé-Hoover chains method [8]. In this approach, several fictitious particles are used and a chain of corresponding equations is solved.

Langevin thermostat

Langevin dynamics in MD simulations assumes that the simulated system is immersed in a “sea” of much smaller fictitious particles [9]. And the Langevin thermostat adds weak random noise to the particle velocities from these fictitious particles. This means that the trajectories do not exactly follow Newton’s equations of motion. If random forces act on each particle in the lattice, then the stochastic Langevin equation for the i -th particle is:

$$m\ddot{x}_i = F_i - m\gamma\dot{x}_i + f_i,$$

where $F_i = -\frac{\partial U(x_j, x_i)}{\partial x_i}$ is the force that determines the Newtonian dynamics of the lattice.

The interaction potential of particles and $U(x_j, x_i)$ is the functional of the potential energy of the pairwise interaction of particles i and j ; γ is the friction coefficient, and f_i is a random force that models random effects from the surrounding heat reservoir on the i -th particle.

To determine random forces, known relationships are used:

$$\langle f_i(t) \rangle = 0; \langle f_j(t) f_i(t') \rangle \delta(t-t') \delta_{i,j} = 2m\gamma k_B T,$$

where the numerical coefficient equal to 2 is determined by the choice of random forces from the normal Gaussian distribution. If in the numerical modeling we move from the continuous consideration to discrete values of time with the integration step Δt , then the time delta function in the left part is replaced by the denominator Δt in the right part. Then the variance of random forces for the Gaussian distribution is

$$\sigma^2 = 2m\gamma k_B T / \Delta t. \quad (2)$$

The random force can also be selected from a uniform distribution of random forces on some interval $[-\tilde{\sigma}, +\tilde{\sigma}]$ (white noise). And the variance of random forces in this case is equal to

$$\tilde{\sigma}^2 = 6m\gamma k_B T / \Delta t.$$

When using the Langevin thermostat, certain restrictions must be observed. Namely, from the very definition of this thermostat it follows that the dispersion of random forces $\langle f(t) f(t) \rangle$ must be significantly less than the dispersion of the “internal” dynamic forces $\langle F(t) F(t) \rangle$ (the system is in a “sea” of small fictitious particles and is subject to weak perturbations of its own dynamics). Otherwise, each of the lattice particles will experience Brownian dynamics, and then information about the lattice’s own dynamics will be lost.

The theoretical foundations of thermalization by the methods considered above are contained in the work [10]. The Langevin and Nosé-Hoover thermostats are analyzed in great detail in the work [11]. The same work describes the use of these thermostats in transport processes.

Collision thermostat

The equations of motion in a collision thermostat (collisional dynamics (CD)) [12, 13] have the form:

$$\begin{cases} \frac{dr_i}{dt} = v_i \\ m_i \frac{dv_i}{dt} = -\frac{\partial U}{\partial r_i} + \sum_k f_{ik} \delta(t - t_{ik}) \end{cases}; i \in [1, N]. \quad (3)$$

These equations combine classical dynamics and collisions with virtual thermostat particles. In equations (3) f_{ik} is a stochastic momentum acting on the i -th particle at time t_{ik} .

The collision thermostat is modeled through elastic stochastic collisions of atoms with virtual particles of the medium of mass m_0 :

$$m_i [v_i(t_k + 0) - v_i(t_k - 0)] = f_{ik}; \quad f_{ik} = 2 \frac{m_0 m_i}{m_0 + m_i} (v_0 - v_i)$$

where the velocities of fictitious particles of the thermostat v_0 obey the Maxwell distribution at temperature T_0 :

$$P(v_0) = \left(\frac{m_0}{2\pi k_B T_0} \right)^{1/2} \exp \left(-\frac{m_0 v_0^2}{2\pi k_B T_0} \right).$$

Collisions occur in accordance with the Poisson distribution, which contains the parameter λ , the frequency of collisions between lattice particles and a fictitious particle per unit time. The probability that k collisions will occur in the time interval $[0, t]$ is determined by the Poisson distribution

$$g_k(t) = \frac{(\lambda t)^k}{k!} \exp(-\lambda t)$$

with the parameter λ , the average number of collisions per unit time. In the time intervals between collisions, the dynamics of each particle obeys Newton's equations, corresponding to the interaction potential within the system.

Thus, to implement the CD method, three parameters m_0 , T_0 , λ are specified.

At each step h of the numerical integration of the motion equations for each atom, in accordance with the Poisson distribution, the number of collisions with virtual particles of the medium is found (the probability that there were no collisions is $g_0(h)$, there was one collision – $g_1(h)$, ...).

THERMALIZATION OF THE LATTICE β -FPUT

The Langevin thermostat is the most widely used in modeling and therefore we will consider its use in more detail using the example of thermalization of the β -FPUT lattice with the energy functional

$$U(y) = \frac{1}{2}y^2 + \frac{\beta}{4}y^4 \quad (4)$$

Where $y_j = x_j - x_{j-1}$ is the difference in the deviations of neighboring particles from equilibrium. Here and further: lattice length is $N = 100$, free boundary conditions. The mass of particles in the lattice site is $m = 13$ Da, which, for concreteness, corresponds to the mass of polyacetylene chain site $-(CH)_n$, the integration step is $\Delta t = 1$ fs. For mass measurement units, it is convenient to use the ratio $1 \text{ Da} \approx 931.5 \text{ MeV}/c^2$. If the speed of light is expressed in $\text{\AA}/\text{fs}$, then $1 \text{ Da} = 103.4 \text{ eV fs}^2 \text{\AA}^{-2}$. Therefore, below we will assume $m = 1344 \text{ eV fs}^2 \text{\AA}^{-2}$. For certainty, $\beta = 1 \text{ eV \AA}^{-4}$ is used. Thus, the following units of energy, length and time are used in the problem: eV, $\text{\AA}$ and fs.

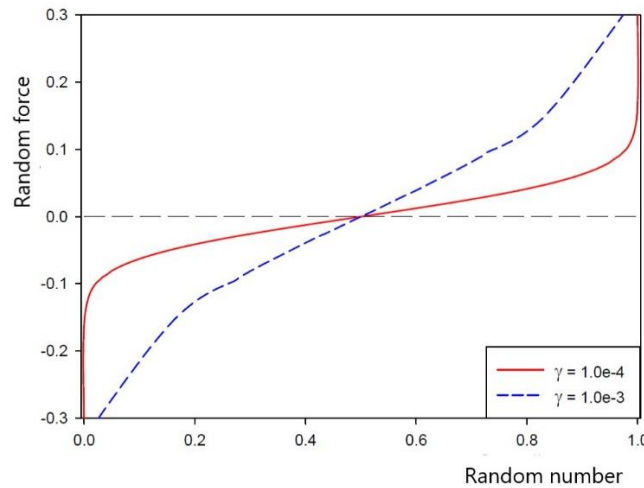


Fig. 1. Cumulative distribution functions of random forces at temperature $T = 100$ K and for two values of the parameter γ : $\gamma = 10^{-3} \text{ fs}^{-1}$ (blue dotted line) and $\gamma = 10^{-4} \text{ fs}^{-1}$ (solid red line).

When using the Langevin thermostat, it is necessary to determine the random forces. For a normal distribution, the random forces are determined through the cumulative distribution function[‡] $\Phi(x) = 1/\sqrt{2\pi} \int_{-\infty}^x \exp(-t^2/2) dt$. For a random number x on the interval $[0, 1]$, the

[‡]The FORTRAN library IMSL contains the program ANORIN(x) that calculates the cumulative function $\Phi(x)$

function $\Phi(x)$ determines the value of a random variable from a normal distribution with a variance equal to one. Then the random force is determined as follows: $f = \sigma\Phi(x)$ and $\sigma = \sqrt{2m\gamma k_B T / \Delta t}$. Figure 1 shows cumulative functions with variances of random forces corresponding to two values of the parameter γ .

The expression for the dispersion of the random force (2) is temperature balanced in terms of the values of the thermostat parameters γ and Δt : an increase in the parameter γ leads to an increase in random forces, but this increase is “quenched” by increased friction; a decrease in the integration step Δt also leads to an increase in random forces, but this is compensated by a smaller transmitted impulse $f\Delta t$. And in a wide range of values of the parameters γ and Δt , the required temperature T_0 is set.

Usually, the standard fourth-order Runge-Kutta method is used to integrate stochastic Langevin dynamics equations. However, more accurate methods are also used [14, 15]. This is a 3o4s2g algorithm which implies integration using the third-order Runge-Kutta method with an integration step divided into four parts and two calls to a random number generator with a Gaussian distribution. Other integration algorithms based on the Runge-Kutta method are also used.

Figure 2 shows the time dependence of temperature for several values of the attenuation parameter γ . These dependences are well approximated by an exponential dependence and the time to reach a stationary temperature value is approximately $\tau_{eq} = \gamma^{-1}$. Temperature fluctuations decrease with decreasing values of γ .

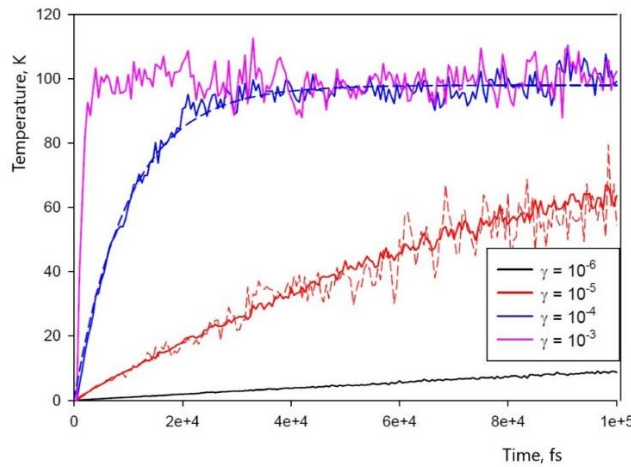


Fig. 2. The dependence of the time of setting the stationary temperature value $T_0 = 100$ K on the time for several values of the parameter γ . The red dotted line for $\gamma = 10^{-5} \text{ fs}^{-1}$ is the temperature along a single MD trajectory. The blue dotted line for $\gamma = 10^{-4} \text{ fs}^{-1}$ is an approximation of the temperature profile by the expression $T(t) = T_0[1 - \exp(-t/\tau)]$, where $\tau = 1/\gamma$. Averaging is carried out over 10 MD trajectories. The values of γ are shown in the inset to the figure.

The total energy of the system can be represented as an expansion over the oscillatory modes of a harmonic oscillator. The condition for the thermalization of the system is the equal distribution of energy by the degrees of freedom. The energy of the k -th vibrational mode in the harmonic approximation is $E^k(t) = m/2 \left\{ [\omega^k \mathbf{q}^k \mathbf{x}(t)]^2 + [\mathbf{q}^k \mathbf{v}(t)]^2 \right\}$ where $\mathbf{q}^k \mathbf{x}(t) = \sum_j q_j^k x_j(t)$ and $\mathbf{q}^k$ is the k -th eigenvector of the tridiagonal harmonic matrix $A(N \times N)$ with matrix elements $A(i, i+1) = A(i+1, i) = -1$. The dispersion relation for the harmonic lattice $\omega^k = \sqrt[3]{G/m} |\sin(ka/2)|$ allows one to find the frequency of the k -th vibrational mode. G is the coupling stiffness in the harmonic approximation. If in the potential β -FPUT $\beta = 1 \text{ eV } \text{\AA}^{-4}$, then at low temperatures the role of anharmonicity is small and $G \approx 1$

$\text{eV } \text{\AA}^{-4}$, a is the bond length. Unless otherwise stated, $a = 1 \text{ \AA}$ and the wavelength of the k -th mode is $\lambda^k = 2N/k$.

The Figure 3 shows the partial energies $E^k(t)$ at different moments of time during lattice heating. The total energy of the system $\varepsilon(t) = \sum_k E^k(t)$, obtained from the expansion in vibrational modes, coincides with the energy of the functional (4) with good accuracy. Equipartition in the energies of vibrational modes is also observed for all energies of the system.

Thermalization in the canonical ensemble is a necessary condition for maintaining temperature constancy when modeling various real dynamic processes, for example, during charge transport. There are two types of fluctuations during thermalization: 1) statistical fluctuations $\sim 1/\sqrt{N}$ and 2) dynamic fluctuations caused by the action of random forces. When carrying out modeling, it is advisable to have an idea of the magnitude of dynamic fluctuations and their possible influence on the mechanism of the processes being studied. For example, when studying the dynamics of a polaron in the PBH model, it turns out that large positive fluctuations are an obstacle to the motion of the polaron [16].

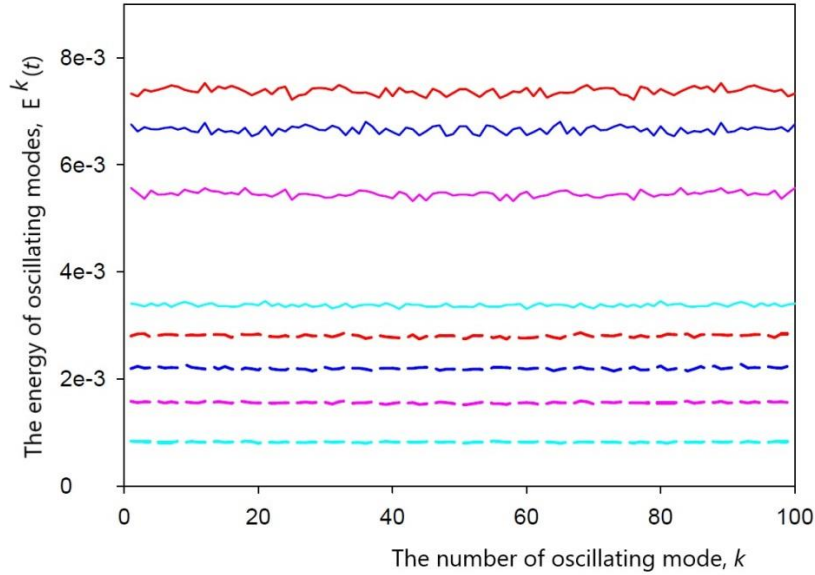


Fig. 3. Partial energies $E^k(t)$ as a function of time. The abscissa axis shows the partial energy number $k \in [1, N]$. The curves are ordered from bottom to top in accordance with the increase in thermalization time ($t = 1, 2, 3, 4, 5, 10, 15, 20$ ps). $T_0 = 100 \text{ K}$, $\gamma = 10^{-3} \text{ fs}^{-1}$.

For a quantitative description, we consider the dispersion of Newtonian forces $\langle FF \rangle$ and the dispersion of random forces $\langle ff \rangle$ depending on the thermostat parameters at $T = 100 \text{ K}$ and $\langle FF \rangle = \frac{1}{MN} \sum_{m=1}^M \sum_{j=1}^N F_j^m(t') F_j^m(t')$ where m is the number of the MD trajectories and M is the total number of trajectories; t' is the moment of time when averaging is performed. The dispersion of random forces is calculated similarly.

If $\gamma = 10^{-3}$, then $\langle FF \rangle \approx 3.5 \times 10^{-2}$ and $\langle ff \rangle \approx 2.24 \times 10^{-2}$. If $\gamma = 10^{-5}$, then $\langle FF \rangle \approx 1.5 \times 10^{-2}$ and $\langle ff \rangle \approx 2.24 \times 10^{-4}$.

The variances of Newtonian forces and random forces are almost the same for $\gamma = 10^{-3}$, but differ by almost two orders of magnitude in the case of $\gamma = 10^{-5}$. Thus, if $\gamma = 10^{-3}$, then the initial assumption that random forces should be much smaller than Newtonian forces due to the interaction potential may be violated.

The phase portrait can serve as a useful qualitative illustration of the lattice dynamics and represents the trajectory of a particle in the coordinate-velocity phase space. The phase portrait of the 50-th particle is shown in Figure 4 for two values of the parameter γ . At $\gamma = 10^{-5} \text{ fs}^{-1}$, a regular, slightly perturbed dynamics is observed. For $\gamma = 10^{-2} \text{ fs}^{-1}$, the phase portrait resembles the Brownian dynamics of a harmonic oscillator ($m\ddot{x} = -kx - \dot{x}m\gamma + f$) for large values of the random force f .

Another criterion of thermalization is a value similar in form to the combinatorial entropy, $S(t) = -\sum_i p_i(t) \ln p_i(t)$, where $p_i(t)$ is the partial share of some average values of dynamic and thermodynamic values at time t : energies of individual vibrational modes, average energy of lattice particles and other parameters [17, 18]. If ideal thermalization is achieved and all partial values are the same, then $S = \ln N$ (N is the number of lattice sites or the number of vibrational modes). If a single vibrational mode is excited, then $S = 0$.

An unconventional method of thermalization of the β -FPUT lattice was used in [19]. Namely, the Langevin thermostat acts only on the two extreme particles of the lattice. The evolution of the state of the system during thermalization was investigated. At the initial stage of thermalization, the lattice is in a nonequilibrium state: in the energy spectrum, there is an asymmetry of energies in favor of short-wave high-frequency vibrational modes. In the dependencies in Figure 3, this would look like a decrease in the energies of vibrational modes for small values of the wave number k compared with larger values of the mode energies for large k .

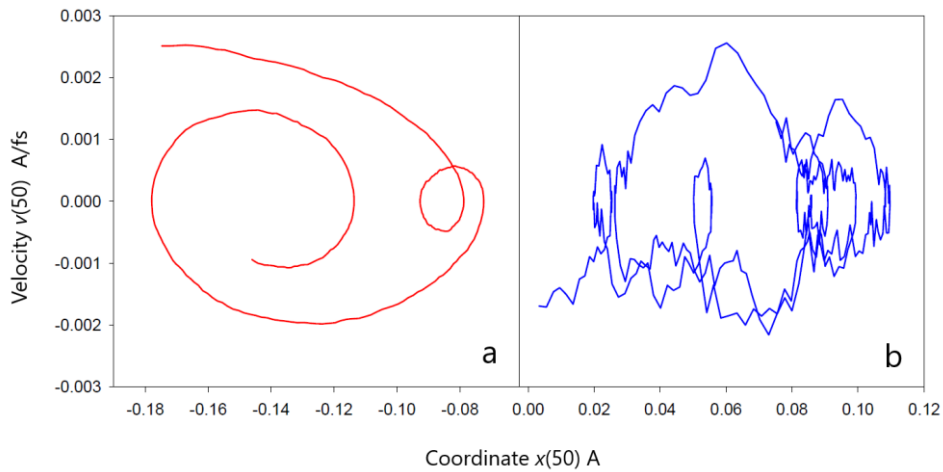


Fig. 4. Phase portraits for two values of $\gamma = 10^{-5} \text{ fs}^{-1}$ (panel a) and $\gamma = 10^{-2} \text{ fs}^{-1}$ (panel b) for the coordinate and velocity of the 50-th particle of the lattice. The phase portraits are shown on the time interval $0 \leq t \leq 300 \text{ fs}$, $T = 100 \text{ K}$.

At the same time, the temperature profile remains almost constant. The energy spectrum equalizes when approaching the equilibrium temperature. The time it takes to establish a steady state of the system depends linearly on the size of the system and decreases with increasing nonlinearity parameter β . The statistical sum is calculated analytically for the β -FPUT lattice. And the thermodynamic parameters of the system found from the statistical sum coincide with high accuracy with the calculated values in the asymptotics $t \rightarrow \infty$.

THERMALIZATION OF PBH LATTICE

The PBH[§] potential was first proposed for practical application in [20]. This potential made it possible to describe an important property of the DNA double helix – its local denaturation with increasing temperature. Although there had been methods for describing

[§]This potential is sometimes called the PBD (Peyrard-Bishop-Dauxois) potential.

denaturation before, only this work was able to describe this process, which occurs in a narrow temperature range. The statistical sum was also calculated there with this potential and the critical denaturation temperature was determined. The sharp peak in heat capacity at $T = 361.5$ K is evidence of a first-order phase transition.

Despite its simplicity, the PBH model has made it possible to describe many important properties of such a complex structure as DNA: melting [21, 22], denaturation [23, 24], and the formation of localized nonlinear excitations [25, 26, 27].

A lattice with a β -FPUT potential can be supplied with arbitrarily high energy due to the type of potential and, accordingly, this system can acquire a very high temperature. A lattice with a PBH potential is very different in this sense, and this is explained by the type of potential:

$$H = \sum_j \frac{1}{2} m \dot{y}_j^2 + V(y_j) + W(y_j, y_{j-1}), \quad (5)$$

where

$$V(y_j) = D(1 - e^{-\alpha y_j})^2 \quad (6)$$

is a Morse potential and

$$W(y_j, y_{j-1}) = \frac{k}{2} \left[1 + \rho e^{-\beta(y_j + y_{j+1})} (y_j - y_{j-1})^2 \right] \quad (7)$$

describes the pairwise interaction of particles. The standard values of the parameters are used [16, 28, 29]: $D = 0.04$ eV, $\alpha = 4.45$ Å⁻¹, $k = 0.04$ eV, $\rho = 0.5$ and $\beta = 0.35$ Å⁻¹. The mass is $m = 3.1 \times 10^4$ eV fs² Å⁻² ($m = 300$ Da). The numerical value of the mass can be reduced by 6 orders of magnitude if the unit of time ps is used instead of fs.

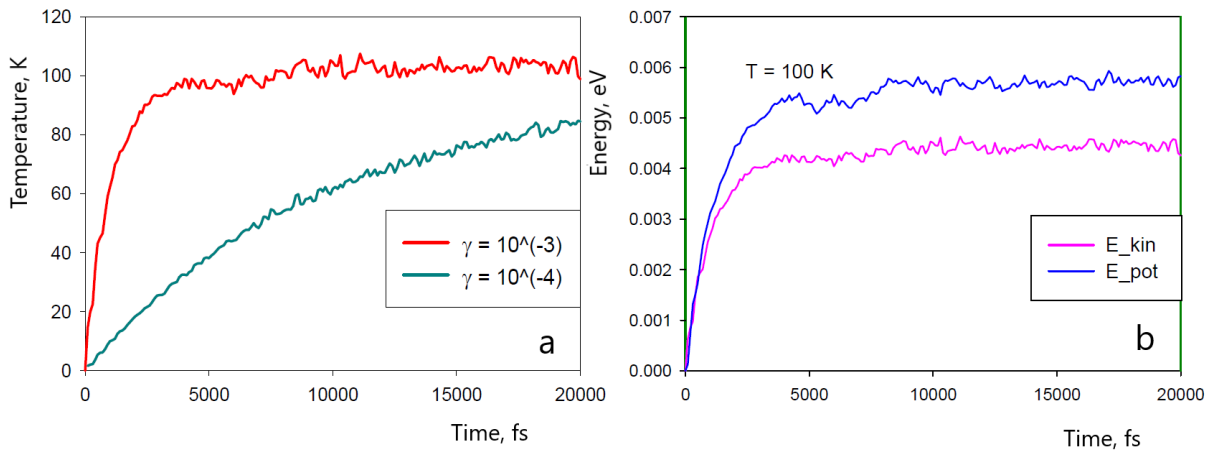


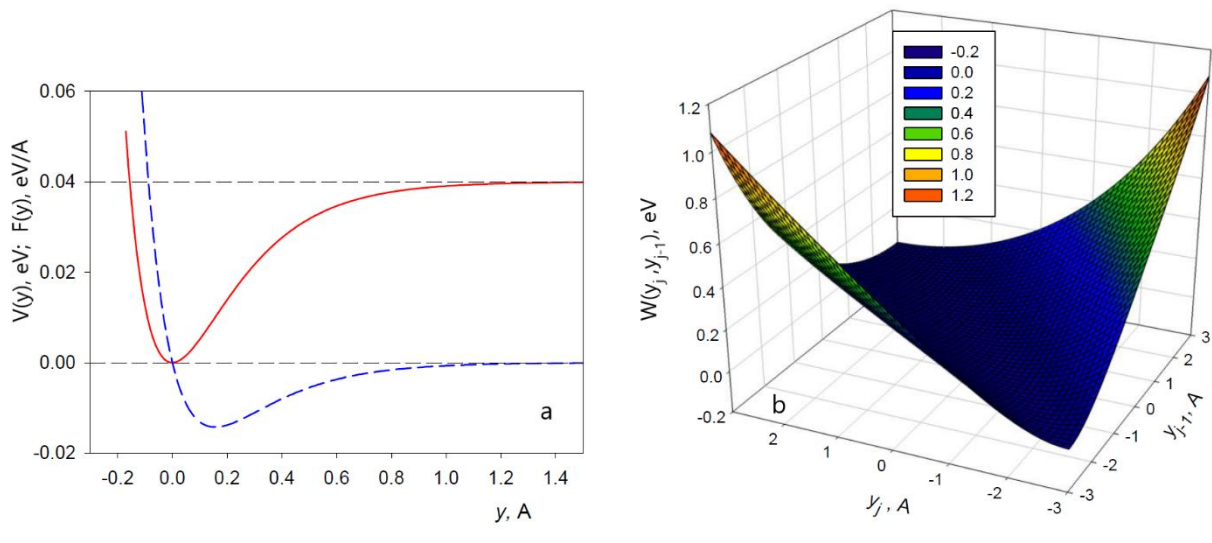
Fig. 5. Panel a: Temperature versus time dependence for two values of the parameter γ (values are shown in the inset). Panel b: Average specific values of kinetic and potential energies as a function of time for $\gamma = 10^{-3}$ fs⁻¹. The curves obtained by averaging over 50 MD trajectories are shown.

Figure 5 shows the change in temperature (panel a) and the average (per a particle) values of kinetic $\langle E_{kin} \rangle$ and potential $\langle E_{pot} \rangle$ energy (panel b). Panel a shows the change in temperature as a function of time for two values of the parameter γ of the Langevin thermostat. The rate at which the steady-state temperature is reached is determined by the parameter γ .

Panel b shows the time dependence of $\langle E_{kin} \rangle$ and $\langle E_{pot} \rangle$. In the steady state at $t > 5000$ fs $\langle E_{pot} \rangle > \langle E_{kin} \rangle$ and this makes it possible to calculate the effective stiffness of the potential. In the particular case where the potential energy of the interaction $V(y)$ is proportional to the n -th

power of the deviation y , i.e. $V(y) = y^2$, the virial theorem [30] takes a simple form: $2\langle E_{\text{kin}} \rangle = n\langle E_{\text{pot}} \rangle$. And from the ratio of the average specific values of the kinetic and potential energies, we can determine the value of the exponent n and it turns out that $V(y) \sim y^{1.6}$, i.e. the effective PBH potential is “softer” than the harmonic one. The exponent n depends on the lattice temperature and the effective potential softens with increasing temperature.

For a better understanding of thermalization, it is advisable to consider the features of the PBH potential. Figure 6,a shows the potential (6) and the corresponding force. Figure 6,b shows a 3D-drawing of the two-particle potential $W(y_j, y_{j-1})$ (7). In this term, the leading role is played by the multiplier $(y_j - y_{j-1})^2$, which minimizes the energy when the coordinates of neighboring particles are equal, regardless of their values. In this figure, this looks like the bottom of a potential valley with equal values of the coordinates y_j and y_{j-1} .



$$F(y) = -\frac{\partial V(y)}{\partial y}$$

Fig. 6. Panel a: Morse potential (red line) and force (dotted line), arising due to deviation of y from the equilibrium position of the potential. Panel b: 3D profile of the potential energy (7).

Such features of the Morse potential as its asymmetry and small depth of the potential well ($D = 0.04$ eV) should be taken into account when performing lattice thermalization. Note that $\frac{1}{2}k_B T \approx 0.013$ eV for $T = 300$ K. The closeness of the values of the potential well depth $D = 0.04$ eV and the energy of thermal vibrations $k_B T$ can create problems associated with the stability of the polaron at physiological temperatures [16].

Similar to the case for the β -FPUT lattice, the $\langle ff \rangle$ and $\langle FF \rangle$ variances were calculated. At $T = 100$ K: $\langle ff \rangle \approx 0.014$ (eV/Å)², $\langle FF \rangle = 0.53$ (eV/Å)² for $\gamma = 10^{-3}$ fs⁻¹ and $\langle ff \rangle \approx 0.013$ (eV/Å)², $\langle FF \rangle = 0.053$ (eV/Å)² for $\gamma = 10^{-4}$ fs⁻¹. At $\gamma = 10^{-3}$ fs⁻¹, the dispersion of random forces is almost 40 times higher than the dispersion of Newtonian forces. For $\gamma = 10^{-4}$ fs⁻¹, the difference between these values is 5.

Formation of bubbles during thermalization of the PBH lattice

The thermalization process of the PBH lattice is associated with the possible formation of bubbles in the DNA structure. The formation of bubbles during the breaking of hydrogen

bonds between two DNA chains is a necessary condition for the functioning of DNA. It is believed that the bubble is a fairly stable structure formed by breaking 3-4 bonds between DNA bases. In nature, the bubble is additionally stabilized by the introduction of water molecules to form hydrogen bonds between the DNA bases of neighboring chains [31].

The two DNA chains are connected by hydrogen bonds, which are parameterized by the deviation of the length of the hydrogen bond from the equilibrium value of y in (5). In MD modeling, the hydrogen bond is represented by the Morse potential (6). Some conclusions follow from Figure 6 for the Morse potential and the corresponding force. First, the force returning the bond length to equilibrium decreases exponentially rapidly with increasing y . For example, for $y = 1 \text{ \AA}$, the restoring force becomes very small. The second conclusion follows from the small depth of the potential well of the Morse potential: $D = 0.04 \text{ eV}$, which is only ~ 3 times greater than the thermal energy (per a degree of freedom) $\frac{1}{2}k_B T \approx 0.013 \text{ eV}$ at $T = 300 \text{ K}$. An additional property of the PBH potential is the presence of term (7), which, due to the multiplier $(y_j - y_{j-1})^2$, stabilizes the lengths of deviations from the equilibrium of neighboring bonds.

It is these features of the potential that lead to the formation of bubbles. Fluctuations in kinetic energy can lead to an increase in the length of the hydrogen bond above $1 \text{ \AA}$. If there is a bond with a similar length in the neighborhood, this will lead to the formation of a metastable structure due to a small restoring force to the equilibrium position. The process of formation and decay of bubbles is reversible.

About the quantum thermostat

Recently, interest has arisen in the so-called quantum thermostats. The idea of the approach is obvious: atoms that make up a particular structure (polymers, DNA), although they are much heavier than electrons, still behave in some cases as quantum objects. This is manifested, for example, in the vibrational spectra of molecules, in which the discreteness of possible vibrational energies is clearly manifested. Thus, there is an obvious contradiction between the widespread classical MD methods, in which energies can take arbitrary values, and the quantum nature of the systems under study.

An obvious consequence of not taking into account the quantization of the energy spectrum is the violation of the theorem on the equal distribution of energy in degrees of freedom, which is one of the foundations of classical statistical physics. This occurs due to the “freezing” of high-frequency oscillations at low temperatures.

If the quantum oscillatory nature of the system is not taken into account, this leads to some incorrect results. The most obvious consequence is an incorrectly calculated heat capacity. It is a well-known fact that in classical MD it is impossible to reproduce the experimental heat capacity. It is overestimated at least twice. The next consequence concerns the results of modeling systems containing different molecules/atoms or consisting of two phases. In this case, the energy is distributed between them incorrectly. The very nature of the motion of the atoms will also be incorrect.

Apparently, the need to take into account the quantum nature in MD modeling was first pointed out in [32], published 15 years ago. At present, quantum thermalization is becoming a subject of increasing interest. The main ideas are implemented in the freely distributed LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) package for MD modeling.

If it becomes necessary to carry out quantum thermalization when modeling a PBH lattice, then the quantization of the Morse potential (energy of quantum levels) is considered in [33], and the solution is expressed in terms of Laguerre polynomials.

CONCLUSIONS

The paper considers thermalization of one-dimensional lattices in a canonical ensemble, when the average temperature of the system is maintained by external sources. As an example, thermalization of a lattice with the β -FPUT potential is considered. The factors influencing the properties of the thermalized lattice are analyzed in detail - the time to reach a steady-state temperature, kinetic energy fluctuations. Quantitative (random force dispersion, equidistribution of energy over the degrees of freedom) characteristics of thermalization, as well as some methods of qualitative description (phase portraits, combinatorial entropy) are described. The nature of thermalization of the PBH lattice is determined by the features of its potential - a small depth of the potential well and an exponentially strong dependence of the Morse potential on the length of the hydrogen bond. Such features of the PBH potential determine the possibility of the existence of bubbles which are vital structures of DNA dynamics. The same properties of the PBH potential can limit the transport of energy and charge due to large geometric fluctuations of the DNA chain. In conclusion, quantum thermalization is briefly considered when the quantum vibrational spectrum is taken into account.

The authors are grateful to N.K. Balabaev for useful advices.

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Received 10.03.2025.

Published 25.04.2025.