Thermal conductivity of the chain with an asymmetric pair interaction

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We provide molecular dynamics simulation of heat transport in one-dimensional molecular chains with different interparticle pair potentials. We show that the thermal conductivity is finite in the thermodynamic limit in the chains with the potential, which allows for bond dissociation. The Lennard-Jones, Morse and Coulomb potentials belong to such type of potentials. The convergence of the thermal conductivity is provided by phonon scattering on the locally stretched loose interatomic bonds at low temperature and by the many-particle scattering at high temperature. On the other hand, the chains with the confining pair potential, which does not allow for the bond dissociation, posses anomalous (diverging with the chain length) thermal conductivity. We emphasize that the chains with the symmetric or asymmetric Fermi-Pasta-Ulam potential or with the combined potentials containing parabolic confining potential all exhibit anomalous heat transport.

I. INTRODUCTION

The heat conductivity of low-dimensional system have attracted intensive studies [1]. The main problem is to derive from first principles, on the atomic level, the thermal conductivity (TC) $\kappa$ as the coefficient, in Fourier law, between the heat flux and temperature gradient, $J = -\kappa \nabla T$. In one-dimensional (1D) case the Fourier law for the chain of $N$ molecules is reduced to the following:

$$J = \kappa (T_+ - T_-)/(N - 1)a,$$  

(1)

where $T_\pm$ is temperatures of left and right chain ends, $a$ is a lattice period. For small temperature difference, $\Delta T = (T_+ - T_-) \ll T = (T_+ + T_-)/2$, Eq. (1) allows to find the dependence of thermal conductivity on the length $L = (N - 1)a$ and temperature of the chain $T$:

$$\kappa(N, T) = J(N - 1)a/(T\delta T), \quad \delta = (T_+ - T_-)/T \ll 1. \quad (2)$$

The Fourier law (1) is fulfilled if the following finite limit exists:

$$\tilde{\kappa}(T) = \lim_{N \to \infty} \kappa(N, T).$$

The chain has a finite TC in this case, while it has the anomalous (diverging with the chain length) TC in the case of $\kappa \to \infty$ for $N \to \infty$.

To date, there are numerous works devoted to the numerical modeling of heat transfer in 1D lattices. Anomalies of heat transport in 1D nonlinear systems are well known since the time of the famous work of Fermi, Pasta, Ulam [2]. In integrable systems (harmonic grid, Toda chain, chain of rigid disks) the heat flux $J$ does not depend on the chain length $L$, therefore the thermal conductivity diverges: $\kappa(L) \sim L$ for $L \to \infty$. Here, the heat transfer is carried out by non-interacting quasiparticles, so the energy is not dissipated during the heat transfer. Non-integrability of the system is a necessary but not a sufficient condition for the existence of the normal thermal conductivity. On the examples of a chain with symmetric potential of the Fermi-Pasta-Ulam (FPU) [3–5], disordered harmonic chain [6–8], diatomic 1D gas of colliding particles [9–11], and the diatomic Toda lattice [12], it was shown that some non-integrable systems can also have infinite (diverging with the system size) thermal conductivity. Here, the thermal conductivity increases as a power function of the length: $\kappa \sim L^\alpha$, for $L \to \infty$, with $0 < \alpha < 1$.

On the other hand, the chain with the on-site potential can have finite thermal conductivity. The convergence of the thermal conductivity with the system size was shown for the Frenkel-Kontorova chain [13, 14], for the chain with the sinh-Gordon on-site potential [15], for the chain with $\phi^4$ on-site potential [16, 17] and for the chain of hard disks with substrate potential [18]. The essential feature of these models is the presence of an external potential, which models the interaction of the chain with the substrate. These systems do not possess the translational invariance and the total momentum is not conserved therein. It has been suggested in [12] that the presence of an external potential plays a key role for the convergence of thermal conductivity in the system. It was conjectured an infinite thermal conductivity for all isolated one-dimensional lattices, where the absence of external potential leads to the conservation of the system total momentum. This hypothesis was refuted in the papers [19, 20], in which it was shown that the isolated chain of coupled rotators (a chain with a periodic interparticle potential) has a finite thermal conductivity.

Anomalous thermal conductivity of isolated chains is connected with a weak scattering of long-wavelength phonons having long mean free paths. A mechanism of effective scattering of long-wavelength phonons should exist for the occurrence of finite thermal conductivity. For the rotator chain [20], such a mechanism is the scattering of phonons by roto-breathers. In recent papers [21, 22] the thermal conductivity of an isolated chain with asymmetric pair inter-particle potential was studied. It is claimed in these papers that with a
certain degree of interaction asymmetry, the thermal conductivity measured in nonequilibrium conditions converges in the thermodynamical limit. The authors of [21, 22] attribute the convergence of the thermal conductivity to the uneven thermal expansion of the asymmetric chain. Without a doubt, the thermal expansion of the chain itself can not be the reason for the convergence of thermal conductivity, because such expansion is present in the chain with an asymmetric Toda potential, which is an integrable system! Modeling of heat transfer in [21] was performed with the help of nonequilibrium MD simulation with the Nose-Hoover heat baths. The deterministic Nose-Hoover thermostat is not intended to simulate heat transfer. Its use leads to modeling of the dynamic system which consists of two attractors connected by a one-dimensional chain [23] and may lead to incorrect results [24]. Also in the works [21, 22] the effective mechanism of the scattering of long-wave acoustic phonons was not found. Dispelling the convergence of long-wavelength phonons providing heat. All this has made necessary to conduct a more detailed modeling of the heat transport in 1D systems.

The aim of this work is to simulate the heat transport in molecular chains with asymmetric potentials of the pair inter-particle interaction in the framework of 1) nonequilibrium molecular dynamics using Langevin thermostat and 2) equilibrium dynamics using the Green-Kubo approach. It will be shown that the chains with unbounded asymmetric potentials of the pair interaction can have finite thermal conductivity. For instance the chains with the asymmetric potential which allow for bond dissociation (similar to the Lennard-Jones and Morse potentials) possess finite thermal conductivity in the thermodynamic limit. A chain with a purely repulsive interaction potentials, like the chain with Coulomb interaction between nearest neighbors, also has final thermal conductivity. Thermal conductivity convergence in such chains is caused by strong (anomalous) Rayleigh scattering of long-wave phonons by the fluctuations of local extension at low temperatures, and by many body scattering at high temperatures. On the other hand, the presence of the inter-particle pair interaction which limits such fluctuations and prevents the transformation of the 1D lattice into a 1D gas of colliding particles, results in anomalous (diverging with the system size) thermal conductivity of the 1D chain. Hence the chains with the FPU potential, either symmetric or asymmetric, and the chains with any combined pair potential which includes the parabolic confining potential, have infinite thermal conductivity in the thermodynamic limit. The reason is that such chains do not allow for the bond dissociation or rupture. From our studies we can conclude that the thermal transport of a one-dimensional chain will be anomalous break if the asymmetric potential of the inter-particle pair interaction grows not slower than the square of the relative distance.

\[ H = \sum_{n=1}^{N} \frac{1}{2} u_n^2 + \sum_{n=1}^{N-1} V(u_{n+1} - u_n - r_0), \]  

where \( u_n \) - dimensionless coordinate of \( n \)-th node, the dot denotes differentiation with respect to the dimensionless time \( t \), \( V(r) \) - dimensionless interaction potential between nearest neighbors normalized terms of \( V(0) = 0, V'(0) = 0, V''(0) = 1, r_0 \) - equilibrium bond length. From now on we assume \( r_0 = 1 \).

To simulate the heat transfer in the chain we will use the stochastic Langevin thermostat. Consider a finite chain of \( N_+ + N + N_- \) links. If the interaction potential \( V(r) \) does not suppose possibility of rupture of the bond, then we take the chain with the free ends, and if it admits — chain with fixed ends. Put the \( N_+ \) right boundary nodes in the Langevin thermostat with temperature \( T_+ \), and \( N_- \) nodes in the left-hand edge thermostat Langevin with a temperature of \( T_- \). The corresponding system of equations of motion of the chain is given by

\[ \dot{u}_n = -\partial H/\partial u_n - \gamma u_n + \xi_n^\pm, \quad n \leq N_+, \]
\[ \dot{u}_n = -\partial H/\partial u_n, \quad n = N_+ + 1, ..., N_+ + N, \]
\[ \dot{u}_n = -\partial H/\partial u_n - \gamma u_n + \xi_n^\pm, \quad n \geq N_+ + N + 1, \]

where \( \gamma = 0.1 \) is relaxation coefficient of the particle velocity, \( \xi_n^\pm \) simulates the interaction with thermostat white Gaussian noise normalized by the conditions

\[ \langle \xi_n^\pm(t) \rangle = 0, \quad \langle \xi_n^\pm(t_1)\xi_n^\pm(t_2) \rangle = 0, \]
\[ \langle \xi_n^\pm(t_1)\xi_n^\mp(t_2) \rangle = 2\gamma T_\pm \delta_{nk}\delta(t_2 - t_1). \]

The system of equations of motion (4) integrated numerically. After the onset of thermal equilibrium chain with thermostats and education stationary heat flow was distributed along the chain temperature \( T_n = \langle u_n^2 \rangle_t \) and the local heat flux

\[ J_n = \bar{a}\langle j_n \rangle_t, \quad \text{where} \quad j_n = -\partial H/\partial u_n V'(u_n - u_{n-1} - r_0), \]
\[ \bar{a} \quad \text{- average value of the bond length at} \quad T = \langle T_+ + T_- \rangle/2 \]

(because of thermal expansion at \( T > 0 \), the average bond length exceeds the equilibrium bond length at \( T = 0; \bar{a} \geq r_0 = 1 \)). The following values were used in the numerical simulation: \( T_\pm = (1 \pm 0.1)T, \gamma = 0.1, N_\pm = 40, N = 20, 40, 80, ..., 20480. \)

This method of thermalization overcomes the problem of the thermal boundary resistance. The distribution of the local energy flux \( J_n \) and temperature profile \( T_n \) along the chain are shown in Figure 1. In the steady-state regime, the heat flux through each link at the central part of the chain should remain the same, i.e., \( J_n = J_n = J_0, N_+ < n < N_+ + N \). This property can be employed as a criterion for the accuracy of numerical modeling and can also be used to determine the characteristic time for achieving the steady-state regime and calculation of \( J_n \) and \( T_n \). Figure 1 suggests that the flux is constant along the central part of the chain thus suggesting we achieved the required regime.
At the central part of the chain, we observe the almost linear gradient of the temperature distribution, so that we can define the coefficient of thermal conductivity as 

$$\kappa(N) = J(N - 1)\bar{a} / (T_{N+1} - T_{N+N}).$$  \hspace{1cm} (5)$$

Thermal conductivity can also be found through the Green-Kubo formula [25]

$$\kappa_c = \lim_{t \to \infty} \lim_{N \to \infty} \frac{1}{NT^2} \int_0^t c(\tau) d\tau,$$  \hspace{1cm} (6)$$

where the flow-stream function correlations $c(t) = \langle J_a(\tau) J_a(\tau - t) \rangle_\tau$, and the total heat flux in the chain $J_a(t) = \bar{a}^2 \sum_j j_a(t)$.

To find the correlation function $c(t)$, we consider a finite cyclic chain with $N = 10^4$ units, fully immersed in the Langevin thermostat with temperature $T$. After the onset of the thermal equilibrium with the thermostat, we disable chain interaction with the thermostat and model further on the dynamics of an isolated thermalized chain. To increase the accuracy of the correlation function measurement, we average the found value over $10^5$ independent realizations of the initial thermalization of the chain.

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Here the question of the convergence of the heat conductivity is reduced to the question of the rate of decay of the correlation function $c(\tau)$ for $\tau \to \infty$. The chain has a finite conductivity if the rate of decrease is sufficient for the convergence of the integral (6) and the anomalous thermal conductivity otherwise.

### III. FERMI-PASTA-ULAM POTENTIAL

We consider here a chain with $\alpha$-$\beta$-FPU pair potential:

$$V(r) = r^2/2 - \alpha r^3/3 + \beta r^4/4.$$  \hspace{1cm} (7)$$

When $\alpha > 0$, the FPU potential function is asymmetric – see Fig. 2. For definiteness, we take the following values of the parameters: $\alpha = 2, \beta = 1$.

The FPU potential does not allow for molecular chain breaking, therefore we consider the chain with free ends. The dependence of the thermal conductivity $\kappa$ on the length of the internal part $N$ is shown in Fig. 3. As can be seen from this figure, the asymmetry of the FPU potential does not result in the convergence of the thermal conductivity, it only decreases the divergence rate. Thus, at temperature $T = 0.05$ in the chain with the symmetric FPU potential (for $\alpha = 0$) the thermal conductivity increases with the length as $N^{0.40}$, while in the chain with the asymmetric FPU potential (with $\alpha = 2$) it increases as $N^{0.16}$. This divergence reduction is caused by the fact that in the chain with asymmetric FPU pair potential a new channel of phonon scattering opens – the scattering of phonons by strongly stretched loose bonds.

Analysis of the behavior of the correlation function $c(t)$ for $t \to \infty$ confirms the divergence of the thermal conductivity in the FPU chain. At $t \to \infty$ correlation function $c(t)$ decreases as a power function $t^{-\delta}$ with the exponent $\delta < 1$, see Fig. 4, curve 1. Therefore the integral in the Green-Kubo formula (6) diverges.
ends. For this purpose, the equations of motion (conductivity can be modeled only for such chains with fixed break and heat flux over them will stop. Therefore the thermal fluctuations. After some time, such chains will necessarily have finite binding energies, the chains with these pair potentials and free edges are not stable with respect to thermal fluctuations. Since the Lennard-Jones (and Morse pair potentials:

\[ V(r) = 4\varepsilon \left\{ \frac{\sigma}{(1 + r)} \right\}^6 - \frac{1}{2}, \]

with the parameter \( \sigma = 2^{-1/6} \) and binding energy \( \varepsilon = 1/72 \), and for the Morse pair potential:

\[ V(r) = \varepsilon \left( \exp(-\beta r) - 1 \right)^2, \]

with the parameter \( \beta = 1/\sqrt{2\varepsilon} = 6 \). For these potentials \( V(0) = 0, V'(0) = 0, V''(0) = 1, \lim_{r \to +\infty} V(r) = \varepsilon \). The characteristic form of these two potentials are shown in Fig. 5.

Since the Lennard-Jones (8) and Morse (9) pair potentials have finite binding energies, the chains with these pair potentials and free edges are not stable with respect to thermal fluctuations. After some time, such chains will necessarily break and heat flux over them will stop. Therefore the thermal conductivity can be modeled only for such chains with fixed ends. For this purpose, the equations of motion (4) should be imposed by the following boundary conditions:

\[ u_1 = 0, \quad u_{N+1} = (N_+ + N_0) \]

with the parameter \( a \geq r_0 \) characterizes the density of the chain \( d = r_0/\alpha \). In these chains strong density fluctuations can occur, so we will take into account the interaction of \( n \)-th particle with the left edge thermostat only if its coordinate satisfies \( u_n(t) < N_+ a \), and the interaction with the right thermostat only if it satisfies \( u_n(t) > (N_+ + N) a \).

The dependence of the thermal conductivity of the chain with the Lennard-Jones pair potential on its length is shown in Fig. 6. We can conclude from the results of the numerical simulation that the chain with the density of \( d = 2/3 \) at low temperatures has a finite thermal conduction. The sequence \( \kappa(N) \) converges at \( T = 0.002 \) and \( T = 0.005 \). The trend of the convergence is observed at high temperatures as well, but the convergence is slower and is not fully realized for the used lengths \( N \leq 10240 \). Equilibrium modeling confirms
FIG. 6: The dependence of the thermal conductivity $\kappa$ on the length $N$ of the internal part of the chain with Lennard-Jones pair potential for chain density (a) $d = 1$ and (b) $d = 2/3$. Dependencies are shown at $T = 0.002$, $0.005$, $0.02$, $0.2$ (curves $1$, $2$, $3$, $4$). Straight line $5$ shows the power law $N^{0.89}$. Curves $6$ and $7$ give the dependencies for the chain with the Morse pair potential at $T = 0.002$ and $T = 0.02$. The horizontal straight lines give the values of the thermal conductivity obtained with the use of the Green-Kubo formula.

For low temperatures, where the thermal transport is provided by phonons, the convergence of the thermal conductivity is caused by Rayleigh phonon scattering at the fluctuations of the local bond stretching (bond dissociation). For the particle density $d < 1$, the loose stretched bonds are present in the lattice and their time of life increases with temperature decrease. As one can see in Fig. 7, there are $3$ or $4$ fluctuations of strong bond stretching with time of life $t_b > 10^3$ in the chain with $N = 1000$ particles at temperature $T = 0.002$ and particle density $d = 1/1.1$. In such a system the phonons will have a finite mean free path, from one loose stretched bond to another.

The phonon thermal conductivity shows the tendency of the convergence in the thermodynamic limit in the chain with particle density $d = 1$. The convergence is slower in such chain than that in the chain with the density $d < 1$. In the chain with the nominal density $d = 1$, the probability of fluctuation of strong bond stretching is lower than in the dilute chain with density $d < 1$.

Temperature dependence of the thermal conductivity $\kappa$ is shown in Fig. 8. At normal density $d = 1$, thermal conductivity is nonmonotonic function of temperature. Thermal conductivity increases both at $T \to 0$ and $T \to \infty$. This is due to the fact that at low temperatures the chain behaves almost like a harmonic chain, which has an infinite thermal conductivity, while at high temperatures it behaves as a gas of rigid disks, which is also characterized by the anomalous thermal transport.

But the situation is changed in the diluted chain with density $d = 2/3$. Here the thermal conductivity increases monotonously with temperature. For $T \to \infty$, the thermal conductivity goes to infinity because the system behaves as a gas of rigid disks. But the thermal conductivity goes to zero...
for $T \to 0$ in such system. It is related with the property of the dilute chain with density $d < 1$ that such chain has fluctuations of strong bond stretching which time of life goes to infinity for $T \to 0$. The phonon transport becomes impossible in this case and the thermal conductivity goes to zero for $T \to 0$ in such a system.

Note that the performed in Ref. [26] modeling of the thermal conductivity of Ar nanowires has shown that the quasi-three-dimensional rod made from the particles interacting through the Lennard-Jones potential has a finite (normal) thermal conductivity. This shows that the convergence of the thermal conductivity, with the system length, is faster in quasi-three-dimensional rod than in one-dimensional chain.

In the chain with Morse pair potential, thermal conductivity shows the same behavior as in the chain of Lennard-Jones, see Fig. 6. Therefore, all the results obtained for the Lennard-Jones chain are also valid for the Morse chain.

V. HYPERBOLIC POTENTIALS

We consider the interaction potentials having the form of a hyperbola with linear asymptotes at $r \to \pm \infty$:

$$V(r) = \left[1 + \frac{1}{2} \delta \left(1 - \tanh r\right)\left(\sqrt{1 + r^2} - 1\right) - \frac{b}{\cosh^2(cx)}\right],$$

(11)

where the parameter $\delta \geq 0$ characterizes the asymmetry of the potential. For $r \to +\infty$ and $r \to -\infty$, the hyperbolic potential (11) has the asymptotes $r = 1$ and $(1 + \delta)(r + 1)$, respectively. For $\delta = 0$ or $\delta = 1$ and $b = 0$, the potential (11) has the form of a symmetric or asymmetric hyperbola (see Fig. 9, curves 1 and 2). The following potential also has the form of asymmetric hyperbola:

$$V(r) = r^2/(2(r + 1)), \quad r > -1.$$

(12)

The potential (12) describes the interaction with the hard core. It is defined only for the relative displacements of $r > -1$. For $r \to -1$, the interaction energy tends to infinity [energy grows like $1/2(r + 1)$], and for $r \to \infty$ potential increases as a linear function ($r - 1)/2$ (see Fig. 9, curve 4). In contrast to the symmetric potential FPU, which is characterized by hard anharmonicity, the hyperbolic potential (11) has a soft anharmonicity. Our modeling shows that thermal transport in the chain with the potential (11) is anomalous. For the symmetric potential (parameters $\delta = 0$, $b = 0$), at temperature $T = 1$ the thermal conductivity $\kappa(N)$ grows as $N^{0.30}$ (see Fig. 10, curve 2), and the correlation function $c(t)$ decays as $t^{-0.84}$ (see Fig. 4, curve 2). The asymmetry of the potential reduces the rate of divergence. For the asymmetric potential (parameters $\delta = 1$, $b = 0$), the thermal conductivity $\kappa(N)$ grows as $N^{0.17}$ (see Fig. 10, curve 3), and the correlation function $c(t)$ decays as $t^{-0.85}$ (see Fig. 4, curve 3). For the symmetric potential with additional well (parameters $\delta = 0$, $b = 1$, $c = 4$), the thermal conductivity $\kappa(N)$ grows as $N^{0.28}$ (see Fig. 10, curve 4), and the correlation function $c(t)$ decays as $t^{-0.58}$ (see Fig. 4, curve 4).

In Fig. 11 we show the dependence of the thermal conductivity $\kappa$ on the length of the central part $N$ of the chain with asymmetric potential with a hard core (12). As one can see, at low temperatures $T = 0.05$ thermal conductivity first increases $\kappa \propto \log(N)$, then the growth rate starts to slow down. At high temperatures, the thermal conductivity is convergent. This is also confirmed by the behavior of the correlation functions. At $t \to \infty$, correlation function decays exponentially, $c(t) \propto \exp(-\lambda t)$, see Fig. 12. Therefore, the Green-Kubo formula (6) gives a finite value of thermal conductivity. Moreover, both approaches (equilibrium and non-equilibrium MD modeling) give the same limiting values for $N \to \infty$, see Fig. 11, which confirms the correctness of the numerical simulation.

VI. TODA POTENTIAL

For comparison, we also consider the Toda pair potential:

$$V(r) = b^{-2}\left[\exp(-br) + br - 1\right],$$

(13)

where the parameter $b > 0$. To be definite, we take the value of the parameter $b = 2.5$ at which at low temperatures Toda potential (13) is well approximated by the asymmetric potential (12), see Fig. 9, curves 4 and 5.

The chain with the Toda pair potential (13) (Toda lattice) is a completely integrable system. The MD simulation shows that the values of the boundary temperatures $T_{N+1}$, $T_{N+N}$ and the value of the heat flux $J$ do not depend on the length of the chain central part $N$ (there is no energy dissipation because the heat transport is performed by non-interacting with
FIG. 10: Dependence of the coefficient of thermal conductivity $\kappa$ on the length $N$ of the central part of two-mass Toda chain (masses $m_1 = 1, m_2 = 2, ...$) at $T = 0.2$ (curve 1), and of the chain with the hyperbolic potential (11) at $T = 1$ with the parameters: $\delta = 0, b = 0$ (curve 2); $\delta = 1, b = 0$ (curve 3); $\delta = 0, b = 1, c = 4$ (curve 4). The straight dashed lines give the power-law dependencies $N^{0.22}$, $N^{0.30}$, $N^{0.17}$ and $N^{0.28}$.

FIG. 11: Dependence of the coefficient of thermal conductivity $\kappa$ on the length $N$ of the central part of the chain with the hard core potential (12) at $T = 0.05, 0.1, 0.2, 0.5$ (curves 1, 2, 3, 4) and chain with Toda potential (13) at $T = 0.2$ (curve 5). The straight lines give the values of the thermal conductivity obtained with the use of the Green-Kubo formula.

FIG. 12: Exponential decrease of the correlation function $c(t)$ for the chain with asymmetric hyperbolic potential (12) at $T = 0.2$.

VII. PURELY REPULSIVE POTENTIALS

Now we consider the thermal conductivity of the chains with purely repulsive potentials:

$$V(\rho) = \frac{1}{\rho},$$

$$V(\rho) = \frac{1}{\rho^{12}},$$

$$V(\rho) = \exp[-b(\rho - 1)^3],$$

$$V(\rho) = \exp[-b(\rho - 1)],$$

$$V(\rho) = \exp[-2b(\rho - 1)] + 2\exp[-b(\rho - 1)]$$

where $\rho$ is a distance between the interacting particles, and the parameter $b > 0$. Purely repulsive is also the following short-range potential:

$$V(\rho) = 0 \text{ for } \rho \geq 1,$$

$$V(\rho) = \exp\{-b[(\rho - 1) + \alpha/(\rho - 1)^2]\} \text{ for } \rho < 1,$$

where parameters $b > 0, \alpha > 0$.

In order to obtain a stable system, we fix the length of the...
chain and consider the chain of $N$ sites with fix ends:

$$u_1(t) \equiv 0, \quad u_N(t) \equiv (N-1)a,$$

(20)

Then the ground state of the chain with a fixed density of $d = 1/a$ will be the homogeneous lattice with period $a$: $u_n = (n-1)a, n = 1, 2, ..., N$, in which the pair inter-particle potential is given by one of the repulsive potentials (14)–(19).

In a chain with a fixed density, the Coulomb repulsion potential (14) can be replaced by the asymmetrical hyperbolic potential:

$$V(\rho) = \frac{1}{\rho} + \frac{\rho}{a^2} - \frac{2}{a} = \frac{\alpha^2}{\rho^2}/(r + a),$$

(21)

where the relative displacement $r = \rho - a$ is introduced. Replacement of the Coulomb potential (14) by the asymmetric hyperbolic potential (21) does not change the system of equations of motion of a chain with fixed ends (20). Therefore one should expect that the chain with a repulsive Coulomb potential has finite thermal conductivity.

Direct modeling of heat transfer has shown that thermal conductivity of the chain with a fixed density converges with the increase of the length, see Fig. 13. Analysis of the behavior of the correlation function also confirms the convergence of the thermal conductivity: at $t \to \infty$ the correlation function $c(t)$ tends to zero exponentially. Both methods of non-equilibrium and equilibrium MD modeling give the same limiting value, $N \to \infty$, of the thermal conductivity. From this we can conclude that the convergence of the thermal conductivity in a lattice with the short-range repulsive potential (19) is provided by the many-particle collisions.

Chain with a repulsive potential (15) also has a finite thermal conductivity. This potential leads to a more rigid collision than the Coulomb potential does. With this potential, the time of pair collision is shorter and hence the effects caused by the many-particle collisions should exhibit weaker, and the thermal conductivity must converge slowly with the length increase. The correlation function $c(t)$ decays in time expo-
the thermal conductivity of the chain with repulsive potential (16) also has the final thermal conductivity. Here, the correlation function \( c(t) \) decays exponentially, and the Green-Kubo formula gives the limiting value of \( \kappa(N) \) for \( N \to \infty \), which coincides with the one given by non-equilibrium simulations, see Fig. 13.

In a chain with a fixed density, pure exponential repulsive potential (17) can be replaced by the Toda potential

\[
V(r) = e^{-br} + \beta e^{-br} - e^{-br} [1 + \beta a] = e^{-br} [\exp(-br) + br - 1],
\]

where \( r = \rho - a \) is the relative displacement. Replacement of the exponential potential (17) by the Toda potential (22) does not lead to a change in the equations of motion in the chain with fixed ends (20). Therefore, the chain with an exponential repulsive potential is completely integrable system and has an infinite conductivity. In the direct simulation of the heat transfer, the values of the boundary temperatures \( T_{N,+1} \) and \( T_{N,+N} \), and the value of the heat flux \( J \) do not depend on the length of the chain between the thermostats \( N \) (the same temperature is set throughout the whole central part of the chain).

Repulsive potential which is a sum of two exponential functions (18) can not be replaced by the Toda potential (22). The presence of the second exponential function in the potential makes the molecular chain to be the non-integrable system. Our MD simulations show that the chain with such repulsive potential has a finite thermal conductivity, and the correlation function decays exponentially. For \( b = 6 \) and temperature \( T = 10 \), the Green-Kubo formula gives the value of the thermal conductivity \( \kappa_c = 77800 \). The dependence of the thermal conductivity \( \kappa \) of the chain length \( N \) is shown in Fig. 16. As one can see, the convergence of the thermal conductivity should be expected at chain length \( N \sim 10^5 \).

**VIII. COMBINED ASYMMETRIC POTENTIALS**

Now we consider the potentials which are the sum of the previously considered asymmetric potentials with the harmonic (parabolic) potential. The addition of the parabolic potential leads to the stabilization of the inter-atomic bonds. Below we study how this stabilizing effects on the thermal conductivity.
conduction of the chain.

The sum of the Toda and the parabolic potentials has the following form:

\[ V(r) = \frac{1}{2}b^{-2}\exp(-br) + br - 1 + \frac{1}{4}r^2, \]  

where the parameter \( b > 0 \), \( r = \rho - 1 \) is the relative displacement. Simulations show that for \( b = 2.5 \) and \( T = 1 \), the thermal conductivity of the chain \( \kappa(N) \) grows as \( \ln(N) \) — see Fig. 17. Such an increase is consistent with the observed behavior of the correlation function: the latter decays slower than \( t^{-1} \), see Fig. 18. Thus, the chain with the combined potential (23) has an infinite thermal conductivity.

The sum of the parabolic potential and the hyperbolic potential with a hard core (12) has the form

\[ V(r) = \frac{1}{4}r^2/(r + 1) + \frac{1}{4}r^2. \]  

(24)

Modeling of the heat transfer in a chain with the combined potential (24) shows that at \( T = 0.5 \) the thermal conductivity \( \kappa(N) \) grows as \( \ln(N) \), see Fig. 17. Such growth is consistent with the time dependence of the correlation function, which decays slower than \( t^{-1} \), see Fig. 18.

The sum of the parabolic and Morse potentials has the form of

\[ V(r) = \frac{1}{2}\varepsilon[\exp(-\beta r) - 1]^2 + \frac{1}{4}r^2, \]  

where the parameter \( \beta = 1/\sqrt{2\varepsilon} \), \( \varepsilon = 1/72 \). MD simulation of the heat transfer at temperatures \( T = 0.05 \) and \( T = 0.5 \) shows that the correlation function \( c(t) \) for the chain with the pair potential (25) decays as a power function of time, \( \propto t^{-0.9} \) at \( t \to \infty \). Because of this, the thermal conductivity of such chain also diverges in the limit of \( N \to \infty \).

The non-smooth vibro-impact potential

\[ V(r) = \frac{1}{2}r^2, \text{ for } r > -1, \text{ and } V(r) = \infty \text{ for } r \leq -1. \]  

(26)

can be approximated by a smooth combined potential:

\[ V(r) = \frac{1}{2}r^2 + 0.001/(r + 1)^2, \]  

(27)

see Fig. 14.

MD modeling of the heat transfer in the chain with a combined asymmetric pair potential (27) shows that at \( T = 1 \) the correlation function \( c(t) \) also decays as a power function, as \( t^{-0.9} \) for \( t \to \infty \). This allows us to conclude that the chain with the vibro-impact interaction potential (26) has an infinite thermal conductivity. Thus, the chains with the combined pair interaction potentials, with a parabolic potential as a component, always are characterized by anomalous heat transport. The form of the potential (26), its parabolicity for small relative displacements, allows one to conclude that the anomalous thermal transport is related here with the long mean free path of small-amplitude phonons.

Analyzing all the simulation results, we can conclude that the asymmetry of the pair potential only does not guarantee the convergence of the thermal conductivity. The chains with the asymmetric potential FPU pair potential (7) and with the asymmetric hyperbolic potential (11) have infinite conductivity. The asymptotic behavior of the interaction potential both in approaching and separating the particles is very important for the convergence of the thermal conductivity in the thermodynamic limit. If the interaction potential has a hard core (interaction energy between two particles tends to infinity when
approaching their centers) and the interaction grows no faster than the distance between the particles in separating them, the chain with such potential will have a finite thermal conductivity. The single-well potentials (8), (12) and purely repulsive potentials (14), (15) belong to such class of pair potentials. Morse potential (9) and the short-range potential (19) do not have hard core, but the chains with these potentials also have finite thermal conductivity. The finite binding energy of the pair potential can result in local bond stretching which strongly scatter phonons. On the other hand, the rapid growth in particles interaction energy in approaching their centers can result in energy scattering in many-particle collisions. The first and second scenarios are responsible for the convergence of the thermal conductivity at low and high temperatures, respectively.

IX. CONCLUSIONS

Our molecular-dynamics simulations show that the one-dimensional chains with unlimited asymmetric pair potentials can have finite thermal conductivity. We show that the thermal conductivity converges in the chains with the Lennard-Jones (8) and Morse (9) potentials, and in the chain with the hyperbolic potential (12). The asymmetric potentials, which lead to the convergence of the thermal conductivity, are characterized by the presence of either a final binding energy, where one branch of the potential is a limited function [Lennard-Jones, Morse, short-potential (19)], or a hard core potential [potentials (12), (14), (15)].

In the chains with fixed ends, the purely repulsive potentials (14), (15), (16) can be reduced to a single-well asymmetric potentials with an asymptotic linear branch. At high temperatures, a chain with such potential may be considered as a one-dimensional gas of particles, interacting through their collisions. An example of a chain with a short-range repulsive potential (19) shows that the finite conductivity of the “gas” is related with the energy dissipation during many-particle collisions. Therefore the chain with repulsive potentials also have a finite conductivity. The exception is the potential with exponential repulsion (17), which can be reduced to the Toda potential (22). Toda lattice is completely integrable system in which the dynamics can always be described by means of non-interacting elementary excitations, and therefore it has an infinite thermal conductivity.

In the combined potentials (23), (24), (25) and (27), the parabolic potential, which stabilizes the bonds, is present. The local strong bond stretching is not possible also in the chain with the FPU potential (7) and the chain with the vibro-impact potential (26). There is no anomalous scattering of phonons at the local stretching at low temperatures, and there is no one-dimensional “gas” of particles, interacting through their collisions at high temperatures. Therefore, the thermal conductivity is divergent in the thermodynamic limit. But the divergence can be very slow and can appear in large lengths only. That is why it is stated in Refs. [21, 22] that the thermal conductivity can converge in the chains with such asymmetric pair potentials. More detailed modeling allows us to unambiguously conclude that he thermal conductivity diverges in such lattices. Therefore the chain with the asymmetric FPU potential always has an infinite thermal conductivity.

Note that the Morse potentials are commonly used in molecular dynamics to describe the stiff valence bonds, and the Lennard-Jones and Coulomb potentials to describe the soft non-valence bonds. Deformation of the valence and torsion angles is described by the limited angular periodic potentials. We have shown that the chain with such potentials have a finite thermal conductivity. Therefore, it is expected that the quasi-one-dimensional molecular systems with such potentials must have a finite thermal conductivity, but the convergence can occur at very large lengths. So far these lengths were not reached in MD simulations of carbon nanotubes [27, 28] and nanoribbons [29, 30], and which makes the impression that the nanotubes and nanoribbons have infinite thermal conductivity. On the other hand the convergence of the thermal conductivity was obtained for more soft quasi-one-dimensional molecular structure, the double helix of DNA [31].

Thus, our numerical simulations show that the chains with unlimited asymmetric potentials that allow the possibility of strong bond stretching (Lennard-Jones, Coulomb and Morse potentials) are characterized by a finite thermal conductivity. The convergence of the thermal conductivity is due to scattering of phonons by strongly stretched bonds at low temperatures, and in result of many-particle collisions at high temperatures. On the other hand, if the pair interactions limit strong local fluctuations and do not allow for strong bond stretching, the chain will have an anomalous thermal conductivity. The thermal conductivity diverges in a thermodynamic limit in a chain with asymmetric FPU potential and in a chain with any combined potential, which has a parabolic potential as a component. We can conclude from our simulations that the thermal conductivity of the chain will diverge if the energy of pair particle interaction grows not slower than the square distance in separating the particles.

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