Normal heat conductivity in chains capable of dissociation

O. V. Gendelman¹ and A. V. Savin²

¹ Faculty of Mechanical Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel
² Semenov Institute of Chemical Physics, Russian Academy of Sciences – Moscow 119991, Russia

PACS 44.10.+i – Heat conduction
PACS 05.45.-a – Nonlinear dynamics and chaos
PACS 05.60.-k – Transport processes
PACS 05.70.Ln – Nonequilibrium and irreversible thermodynamics

Abstract – The paper suggests a resolution for recent controversy over convergence of heat conductivity in one-dimensional chains with asymmetric nearest-neighbor potential. We conjecture that the convergence is promoted not by the mere asymmetry of the potential, but due to ability of the chain to dissociate. In other terms, the attractive part of the potential function should approach a finite value as the distance between the neighbors grows. To clarify this point, we study the simplest model of this sort – a chain of linearly elastic disks with finite diameter. If the distance between the disk centers exceeds their diameter, the disks cease to interact. Formation of gaps between the disks is the only possible mechanism for scattering of the oscillatory waves. Heat conduction in this system turns out to be convergent. Moreover, an asymptotic behavior of the heat conduction coefficient for the case of large densities and relatively low temperatures obeys simple Arrhenius-type law. In the limit of low densities, the heat conduction coefficient converges due to triple disk collisions. Numeric observations in both limits are grounded by analytic arguments. In a chain with Lennard-Jones nearest-neighbor potential the heat conductivity also saturates in a thermodynamic limit and the coefficient also scales according to the Arrhenius law for low temperatures. This finding points on a universal role played by the possibility of dissociation, as convergence of the heat conduction coefficient is considered.

Heat conduction in low-dimensional systems has attracted a lot of attention and has been a subject of intensive studies [1,2]. The main objective here is to derive from first principles (on the atomic-molecular level) the Fourier law – proportionality of the heat flux to the temperature gradient $J = -\kappa \nabla T$, where $\kappa$ is the heat conduction coefficient. To date, there exists quite extensive body of works devoted to the numerical modeling of the heat transfer in the one-dimensional chains. Anomalous characteristics of this process are well-known since celebrated work of Fermi, Pasta and Ulam [3]. In integrable systems (harmonic chain, Toda lattice, the chain of rigid disks) the heat flux $J$ does not depend at all on the chain length $L$, therefore, the thermal conductivity formally diverges. The underlying reason for that is that the energy is transferred by non-interacting quasiparticles and therefore one cannot expect any diffusion effects. Non-integrability of the system is a necessary but not sufficient condition to obtain the convergent heat conduction coefficient. Well-known examples are Fermi-Pasta-Ulam (FPU) chain [4,5], disordered harmonic chain [6,7], diatomic 1D gas of colliding particles [10,12] and the diatomic Toda lattice [13]. In these non-integrable systems also have divergent heat conduction coefficient; the latter diverges as a power function of length: $\kappa \sim L^{\alpha}$, for $L \to \infty$. The exponent lies in the interval $0 < \alpha < 1$.

On the other side, the 1D lattice with on-site potential can have finite conductivity. The simulations had demonstrated the convergence of the heat conduction coefficient for Frenkel-Kontorova chain [14,15], the chain with hyperbolic sine on-site potential [16], the chain with $\phi^4$ on-site potential [17,18] and for the chain of hard disks of non-zero size with substrate potential [19]. The essential feature of all these models is existence of an external potential modeling the interaction with the surrounding system. These systems are not translationally invariant, and, consequently, the total momentum is not conserved. In paper [14] it has been suggested that the presence of an external potential plays a key role to ensure the convergence of the heat conductivity. This hypothesis has been disproved...
in works [20, 21], where it was shown that the isolated chain of rotators (a chain with a periodic potential interstitial interaction) has a finite thermal conductivity. Some recent studies [22, 23] claim that the heat conduction is convergent in some model chains with an asymmetric potential of interaction. In particular, this claim addressed α-FPU model and a chain of particles with Lennard-Jones (LJ) interaction. Results [24, 25] deny these claims for α-FPU model; however, they do not address the LJ chain. More detailed results in recent paper [26] indicate that the role of the dissociation directly.

In generic nonlinear potential it seems very difficult to distinguish between various factors which effect the heat conductivity, and to filter out the effects related to a topology of the potential function. To overcome this difficulty, we consider a chain of elastic disks. In the ground states for high density this system is in fact a linear chain. So, the gap formation is the only possible mechanism of the phonon scattering. Thus, this model allows one to study the role of the dissociation directly.

The model chain comprises \( N \) one-dimensional “disks” with elastic compressive nearest-neighbor interaction. In other terms, the system Hamiltonian is expressed as

\[
\mathcal{H} = \sum_{n=1}^{N} \frac{p_n^2}{2M} + \sum_{n=1}^{N-1} U(x_{n+1} - x_n),
\]

where \( M \) is the mass of each particle, \( x_n \) is a coordinate of the center of \( n \)-th disk, \( p_n \) – its momentum. The potential of interaction in this model is defined as:

\[
U(r) = \begin{cases} 
K(r - D)^2/2, & r < D \\
0, & r \geq D
\end{cases},
\]

where \( K \) – stiffness of the disks and \( D \) – their diameter. The neighboring disks repulse each other linearly, when their centers are at a distance less than \( D \). In order to keep a ”numeric” density (a number of the disks at unit length) constant, we adopt that terminal disks are fixed: \( x_1(t) \equiv 0, \ x_N(t) \equiv (N - 1)a \). Here \( a \) is average length of the link between the neighboring particles.

Introducing dimensionless time \( \tau = t\sqrt{K/M} \), displacements \( u_n = x_n/a \) and energy \( H = \mathcal{H}/Ka^2 \), we arrive to the following non-dimensional Hamiltonian:

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

where apostrophe denotes differentiation with respect to \( \tau \). Non-dimensional potential of interaction is described as

\[
V(\rho) = \begin{cases} 
(\rho - d)^2/2, & \rho < d \\
0, & \rho \geq d
\end{cases}.
\]

Parameter \( d = D/a \) is related to a ”packing density” of the disks (numeric density is always unit, as it was explained above).

Potential \( V(\rho) \) has a discontinuity of the second derivative. To avoid numeric complications, we approximate it by smoothened potential in a form

\[
V_h(\rho) = \left[\sqrt{(\rho - d)^2 + h} - (\rho - d)\right]^2/8.
\]

Value of parameter \( h \) determines the accuracy of the smoothening. A limit \( h \to 0 \) corresponds to non-smooth potential \( V(\rho) \). For simulations at relatively high temperatures \( T \geq 0.09 \) we use \( h = 0.01 \) and for lower temperatures \( -h = 0.0005 \). The quality of approximation \( V_h(\rho) \) for higher value of \( h \) is illustrated in Fig. 1.

In order to simulate the heat transfer in this model, we used Langevin stochastic thermostat. To verify the results, we used both commonly accepted methods for computation of the heat conduction coefficient — based on stationary heat transfer and on linear response theory. To simulate the stationary heat transfer, we considered the chain with Hamiltonian \( (1) \) and potential \( (2) \), comprising in general \( N_+ + N_+ + N_- \) disks. Terminal fragments of the chain with \( N_+ \) and \( N_- \) particles are permanently attached.

\[\text{Fig. 1: (Color online) Comparison between the potential } V(\rho) \text{ (curve 1) and smoothened potential } V_h(\rho) \text{ with } h = 0.01 \text{ (curve 2).}\]
Then, we computed the values of average local temperature at free part of the chain has been observed. Velocity Verlet method. After initial transient, stationary heat flux at free middle part of the chain; this part comprises \( N \) particles. To be even more specific, we simulated numerically the following system of dynamic equations:

\[
\begin{align*}
    u'_n &= -\partial H/\partial u_n - \gamma u'_n + \xi^+_n, \quad 1 < n \leq N_+,
    
    u''_n &= -\partial H/\partial u_n, \quad N_+ < n \leq N_+ + N, \\
    u''_n &= -\partial H/\partial u_n - \gamma u'_n + \xi^-_n, \\
        &\quad N_+ + N < n < N_+ + N + N_-.
\end{align*}
\]

(6)

Here \( \gamma \) is a relaxation coefficient, \( \xi^\pm_n \) is a white Gaussian noise, normalized by the following conditions:

\[
\begin{align*}
    \langle \xi^+_n (\tau) \rangle &= 0, \quad \langle \xi^+ (\tau_1) \xi^- (\tau_2) \rangle = 0, \\
    \langle \xi^- (\tau_1) \xi^- (\tau_2) \rangle &= 2\gamma T_\xi \delta_{nk} \delta (\tau_1 - \tau_2).
\end{align*}
\]

System of equations (6) was integrated numerically by Velocity Verlet method. After initial transient, stationary heat flux at free part of the chain has been observed. Then, we computed the values of average local temperature defined as \( T_n = \langle u'_n \rangle_\tau \) and of average local heat flux \( J_n = \langle j_n \rangle_\tau \), where \( j_n \) denotes an instantaneous local heat flux:

\[
    j_n = (u_{n+1} - u_n)(u'_n + u'_{n+1})F(u_{n+1} - u_n)/2 + u'_n h_n,
\]

\[
    F(\rho) = -\partial V_\rho / \partial \rho \quad \text{and} \quad h_n = [u'^2_n + V_n(u_{n+1} - u_n) + V_n(u_n - u_{n-1})]/2
\]

(see [1]). All time averages were defined as

\[
    \langle f \rangle_\tau = \lim_{\tau \to \infty} \tau^{-1} \int_0^\tau f(\tau) d\tau.
\]

In all simulations, we will use the following parameter values: \( T_\pm = (1 \pm 0.05)T, \quad \gamma = 0.05, \quad N_\pm = 40, \quad N = 20, 40, \ldots, 2560. \)

As it is illustrated in Fig. 2, the heat flux \( J = J_n \) through the central (free) segment of the chain was stationary (cite-independent). The heat conduction coefficient has been then evaluated as

\[
    \kappa(N) = J(N - 1)/(T_{N+1} - T_{N+N}).
\]

Fig. 2: (Color online) Distribution of (a) average heat flux \( J_n \) and (b) local temperature \( T_n \) in the chain of elastic disks with \( d = 1 \) and \( N_\pm = 40, N = 320, T_+ = 0.105, T_- = 0.095 \).

Straight red line approximates the linear temperature gradient which was used for evaluation of the heat conduction coefficient \( \kappa(N) \).

Fig. 3: (Color online) Dependence of heat conduction coefficient \( \kappa \) on the length of free internal chain fragment \( N \) for the model of elastic disks with (a) \( d = 0.1 \) and (b) \( d = 1 \) for temperatures \( T = 0.1, 1, 10 \) (curves 1, 2, 3 respectively). Horizontal lines correspond to the values of the heat conduction coefficient obtained with help of Green-Kubo formula [5].
We consider a cyclic chain consisting of $N$ realizations of the initial thermal distribution. To improve the accuracy, the results were averaged over $10$ thermostat and Hamiltonian dynamics is simulated. To achieve the thermal equilibrium, the system is detached from the thermostat. This result is illustrated in Fig. 4. Both tests yield very close results for large values of $(d-1)^2$. This result is confirmed in Fig. 3.

Arrhenius formula. The velocity of the oscillatory waves may be crudely estimated as a sound velocity and is equal to unity in our non-dimensional model. Then, the heat conduction coefficient may be crudely estimated as:

$$\kappa \approx \exp[\alpha(d-1)^2/T].$$

Scaling of $\ln \kappa$ with $(d-1)^2$ and $T^{-1}$ is presented in Figs. 4 and 6. One can see that the results nicely correspond to estimation (10) for $d > 1$ and relatively large temperatures. This result confirms our understanding of the reasons for normal heat conductivity in this system.

The case of loose packing of the disks, corresponding to $d < 1$, also deserves special attention. As the temperature is relatively small, the disks will move free for most of the time. Due to linear elastic interaction the model, the time of each binary collision $\tau_c$ between the disks will not depend on the temperature and the density: $\tau_c = \pi$. The collisions are elastic. If the collisions would be only binary, the momentum of colliding particles would be simply exchanged in each collision. Therefore, the system would be equivalent to a billiard of particles with equal masses on a line, and therefore would be completely integrable. Thus, finite heat conduction coefficient is intimately related to triple (and higher-order) collisions. One can adopt (in a limit of very loose packing, $d << 1$) that a mean free path $\lambda_{imp}$ of an impulsive excitation transferred through the binary collisions is inversely proportional to a probability that the disk will hit a system of two already interacting disks. This probability can be estimated as the ratio of the times of the interaction and the free flight. The latter, in turn, can be estimated as $\tau_0 = (1-d)/\sqrt{T}$ (average velocity of the disk $v \sim \sqrt{T}$). Then, the heat conduction coefficient for small temperatures and small $d$ may be crudely estimated as:

$$\kappa \sim v\lambda_{imp} \sim v\tau_0/\tau_c \sim (1-d)/\pi.$$
Fig. 6: (Color online) Dependence of \( \ln(\kappa) \) on inverse temperature \( T^{-1} \) for the disk diameters \( d = 0.1 \), \( d = 1 \) and \( d = 1.5 \) (curves 1, 2, 3 respectively). Upper straight line gives Arrhenius scaling for case \( d = 1.5 \). Lower straight line gives value of heat conductivity in limit \( T \to 0 \) for case \( d = 0.1 \).

Equation (10) predicts that the heat conduction coefficient will not depend on the temperature in the limit of loose packing. Numeric simulation completely confirms this prediction – see Fig. 6.

The chain with \( d = 1 \) is an intermediate case between the two limits described above. Formation of the oscillatory waves is hardly possible, since the energy required for the gap formation is zero. From the other side, the free motion of the disk is also largely suppressed. In this case, as it seems, the heat conduction coefficient will weakly depend on the temperature, as it is illustrated in Fig. 6. The value of the heat conduction coefficient in this case is close to \( \kappa = 20 \) in all temperature diapason. The heat conductivity in similar model for this degenerate case has been presented in paper [27]. There they reported the value \( \kappa = 2 \). It seems that this discrepancy is related to Nose-Hoover thermostats used in [27] for the non-equilibrium simulations. As it is well-known, this choice of the thermostats can easily lead to artifacts.

The chain of elastic disks is in a sense unique model – the dissociation is the only possible mechanism of the phonon scattering. However, in more complicated nonlinear chains the role of the dissociation might be less profound, since there are other mechanisms of the phonon scattering – just due to the nonlinearity of the interaction potential. To shed a light on a role of the possibility of dissociation, we simulate the heat conduction in the Lennard-Jones chain with the nearest-neighbor potential

\[
U(x_{n+1} - x_n) = 4\varepsilon [(\sigma/(x_{n+1} - x_n)^6 - 1/2)]^2
\]

with \( \sigma = 2^{-1/6} \) and energy of coupling \( \varepsilon = 1/72 \).

The stationary heat transfer has been simulated according to the protocol described above, with \( N = 40 \), \( N = 2560 \), \( T_T = T(1 \pm 0.1) \). Results of this simulation are presented in Fig. 7.

These results demonstrate Arrhenius-type behavior of the heat conduction coefficient in the limit of low temperatures also for the LJ chain. In the chain of elastic disks such behavior may be attributed to the phonon scattering related to the dissociation. Thus, one can conjecture that also in the LJ chain the convergence of the heat conduction coefficient is related to the possibility of dissociation. In the limit of high temperatures the heat conduction coefficient sharply increases. This observation can be related to strong repulsive core of the LJ potential, which plays main role in the case of relatively high temperatures.

To conclude, we demonstrate that finite coupling energy of the neighboring particles in the model chain can play decisive role in providing the convergent heat conduction. This statement is completely clarified for simple model of linearly elastic disks, and obtain certain support for the model of LJ particles, at least for the case of low temperatures. Notably, very simple considerations related to the mean free path and average velocity of elementary excitations, are sufficient to describe the asymptotic behavior of the heat conduction coefficient. It seems the nonlinearity of the potential, related to the possibility of dissociation, is "strong" enough to make the heat conduction to conform to these well-known models.

***

The authors are grateful to Israel Science Foundation (grant 838/13) for financial support. A. V. S. is grateful to the Joint Supercomputer Center of the Russian Academy of Sciences for the use of computer facilities.

REFERENCES

[1] Lepri S., Livi R. and Politi A., Physics Reports, 377

p-5
[2] Li N., Ren J., Wang L., Zhang G., Hanggi P. and Li B., Rev. Mod. Phys., 84 (2012) 1045.

[3] Fermi E., Pasta J. and Ulam S., Studies of non linear problems (Los Alamos Rpt LA.1940) 1955.

[4] Lepri S., Livi R. and Politi A., Phys. Rev. Lett., 78 (1997) 1896.

[5] Lepri S., Livi R. and Politi A., Physica D, 119 (1998) 140.

[6] Lepri S., Livi R. and Politi A., Europhys. Lett., 43 (1998) 271.

[7] Rubin R. and Greer W., J. Math. Phys., 12 (1971) 1686.

[8] Casher A. and Lebowitz J.L., J. Math. Phys., 12 (1971) 1701.

[9] Dhar A., Phys. Rev. Lett., 86 (2001) 5882.

[10] Dhar A., Phys. Rev. Lett., 86 (2001) 3554.

[11] Savin A. V., Tsironis G. P. and Zolotaryuk A.V., Phys. Rev. Lett., 88 (2002) 154301.

[12] Grassberger P., Nadler W. and Yang L., Phys. Rev. Lett., 89 (2002) 180601.

[13] Hatano T., Phys. Rev. E, 59 (1999) R1.

[14] Hu B., Li B. and Zhao H., Phys. Rev. E, 57 (1998) 2992.

[15] Savin A. V. and Gendelman O. V., Phys. Rev. E, 67 (2003) 041205.

[16] Tsironis G. P., Bishop A. R., Savin A. V. and Zolotaryuk A. V., Phys. Rev. E, 60 (1999) 6610.

[17] Hu B., Li B., and Zhao H., Phys. Rev. E, 61 (2000) 3828.

[18] Aoki K. and Kuznezov D., Phys. Lett. A, 265 (2000) 250.

[19] Gendelman O. V. and Savin A. V., Phys. Rev. Lett., 92(7) (2004) 074301.

[20] Giardina C., Livi R., Politi A. and Vassalli M., Phys. Rev. Lett., 84 (2000) 2144.

[21] Gendelman O. V. and Savin A. V., Phys. Rev. Lett., 84 (2000) 2381.

[22] Zhong Y., Zhang Y., Wang J. and Zhao H., Phys. Rev. E, 85 (2012) 060102(R).

[23] Chen S., Zhang Y., Wang J. and Zhao H., arXiv:1204.5933v3 [cond-mat.stat-mech] 15 Oct 2012.

[24] Das S. G., Dhar A. and Narayan O., arXiv:1308:5745v1 [cond-mat.stat-mech] 26 Aug 2013.

[25] Wang L., Hu B. and Li B., Phys. Rev. E, 88 (2013) 052112.

[26] Savin A. V. and Kosevich Y. A., arXiv:submit/0761690 [cond-mat.stat-mech] 17 Jul 2013.

[27] Li H. and Xin X., arXiv:1201.4171v1 [cond-mat.stat-mech] 23 Jul 2012.