

Effect of an Isotopic Impurity on the Energy Flow in a System of One-Dimensional Coupled Harmonic Oscillators

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linear Schröd- of coupled harmonic oscillators is investigated by means of the ingner coordinates. Assuming such an initial canonical ensemble that half the system is at temperature T and other half at temperature zero, the correlation functions of particles in the system are calculated as functions of time. Thus, it is shown that the average kinetic and potential energies of each particle in the infinitely large system approach different stationary values in both sides of the impurity atom, and that the system approach a stationary state with a gap of energy distribution along the system at the impurity site. This result agrees with that obtained by Kashiwamura and Teramoto by means of trigonometric eigenfunctions of the dynamical system.

The elements of position-velocity correlation matrix are also calculated. The energy flow in the large system is derived from these, and it is shown that even after a sufficiently long time the finite energy flow still exists at every point of the system though there is no temperature gradient at that point.

It should be mentioned, however, that the method we used here is easier to calculate and simpler by far than that by means of the trigonometric eigenfunctions of the dynamical system.

1. PRELIMINARIES

Since the early work of Poincaré¹⁾, Fermi²⁾, and others³⁾, it has been a long standing desire to unify particle mechanics and statistical mechanics by exhibiting a mechanical system whose exact solution can be shown to yield an approach to thermodynamic equilibrium. Due to their work, physicists tend to believe that weakly coupled nonlinear systems will exhibit the ergodic behavior considered necessary for an approach to thermodynamic equilibrium. In accepting ergodicity, however, we should give up almost all hope to have analytic solution of the system considered. In this case, the equations of motion of the system become to be incredibly com-

1) H. Poincaré, *Méthodes Nouvelles de la Mécanique Céleste* (Gauthier-Villars, Paris, 1892).

2) E. Fermi, *Zeits. F. Physik* 24 261. (1923).

3) cf. D. ter Haar, *Elements of Statistical Mechanics* Appendix 1 (Rinehart and Co., New York, 1954).

plicated, and we are obliged to make computations by electronic computers^{4,5}).

To their surprise, Fermi et al.⁴) found that their nonlinear oscillator systems yielded very little energy shearing at all and did not exhibit ergodic behavior. The result obtained by Ford and Waters⁵) by means of computer also showed that their nonlinear systems have many features in common with linear systems. In particular, after perturbation theory⁶) their systems are unlikely to be ergodic, even though they are energy sharing oscillator systems.

On the other hand, due to the work of Debye⁷) and Peierls⁸) on the heat conduction in crystals, as is well known, the existence of anharmonicities in the interatomic force is considered necessary to yield a finite thermal conductivity in crystals. They introduced the concept of mean free path of phonons, being a measure of the coupling between normal modes brought about by the anharmonicity involved in the Hamiltonian of the system.

The nonlinear oscillator systems of Peierls⁸) on lattice thermal conductivity however, make us reluctant to believe that his systems do not exhibit an approach to thermodynamic equilibrium. Up to the present, we have a growing amount of evidence that many physically interesting systems are not ergodic. For example, Resibois and Prigogine⁹) have found constants of motion for gas systems. Kolmogorov¹⁰) has shown that his more general nonlinear systems are not ergodic.

Linear systems nevertheless, have been investigated from the view-point of statistical dynamics of irreversible phenomena especially in the fields of lattice vibrations and rheology. The statistical dynamical approach to the **stationary state** in the linear system gives much information and instructive fundamental concept on the irreversibility of a statistical ensemble.

If one gives up nonlinearity and accordingly ergodicity, then one can treat oscillator systems completely analytically. The ensemble of harmonic oscillators seems to be the only one of the many body systems with strong coupling between particles which provides analytical and statistical calculations.

Klein and Prigogine¹¹) took linear systems of harmonic oscillators, calculated the correlation functions, and showed that their systems approach finally a **stationary state**, where the energy of the systems is a constant of motion. Hemmer¹²), Teramoto¹³), and Takizawa and Kobayasi¹⁴) discussed heat flow in a linear system of harmonically coupled oscillators. They showed that the large system of oscillators approach finally a **stational state**, but **not an equilibrium state**. Starting from such an ensemble that half of the system is at temperature zero, while other half

4) E. Fermi, J. Pasta, and S. Ulam, Los Alamos Sci. Lab. Report. IA-1940 (1955)

5) J. Ford and J. Waters, Journ. Math. Phys. 4 1293, (1963).

6) J. Ford, J. Math. Phys. 2 387, (1961).

7) P. Debye, *Vorträge über die Kinetische Theorie der Materie und der Elektrizität* (Teubner, Berlin, 1914).

8) R. Peierls, *Annalen der Physik* 3 1055, (1929).

9) P. Resibois and I. Prigogine, *Bullet. Acad. Roy. Belg. Class Sci.* 46 53, (1960).

10) A. N. Kolmogorov, *Proc. International Congress Math. Amsterdam Vol. 1* p. 315 (North Holland Publ. Co., Amsterdam 1957); cf. J. Moser, *Math. Rev.* 20 675, (1959).

11) G. Klein and I. Prigogine, *Physica* 19 1053, (1953).

12) P.C. Hemmer, *Det Fysiske Seminar I Trondheim No. 2* 1, (1959).

13) E. Teramoto, *Progress Theoret. Phys.* 28 1059, (1962).

14) E. I. Takizawa and K. Kobayasi, *Chinese Journ. Phys.* 1 59, (1963).

at temperature T , they showed that the average values of the potential and kinetic energies of each particle in a large system approach the same stationary value at the final state, *i.e. after* infinitely long time. This means that the microscopic local temperatures at any point throughout the system approach the same stationary value and there is no temperature gradient in the system at the final state. While, it is shown also that the energy flow¹⁴⁾ still exists at every point of the system at this final state. Due to these work on the re-examination of the problems of energy flow in the one-dimensional harmonic lattice, it seems to be justified that the harmonic model is incapable of describing the phenomena of heat conduction in a system of coupled oscillators. However, it is not yet clear¹⁵⁾ how the anharmonic coupling plays essential rôle in the fundamental molecular kinetic theory of heat conduction. Rubin¹⁶⁾ investigated the heat flow in a harmonic lattice with arbitrary distribution of two kinds of isotopes by means of machine calculation.

Meixner¹⁷⁾, Kashiwamura and Teramoto¹⁸⁾, Hemmer¹²⁾, Turner¹⁹⁾, Rubin²⁰⁾, and Mazur and Montroll²¹⁾ investigated also the model of linear chain with external force, or with a heavy mass. They treated the chain by means of normal modes or Laplace transform of the solutions of equations of motion of the system, from the view-point of special interest of thermal fluctuation, heat conduction, or recurrence time. In the previous paper¹⁴⁾, the present authors took ' a one-dimensional harmonic lattice and investigated heat flow in the system by means of the Schrödinger coordinates.

There the emphasis is laid to elucidate the superiority of using the Schrodinger coordinates, so that we can take explicitly into account the initial conditions in the solutions of dynamical equation of the one-dimensional harmonic lattice.

In the present paper, the authors show that if we want to make study of a one-dimensional lattice with isotopic impurities, we can also use the Schrodinger coordinates conveniently. The dynamical solutions with initial conditions are easily obtained by means of these coordinates. In these solutions the initial conditions are seen explicitly. While, instead, if we take ' normal mode expressions of the solutions of the dynamical system, the initial conditions can not be seen very explicitly in the expressions of the dynamical solutions. Then, statistics is introduced in the initial conditions, and we persue the timal behavior of the system hereafter. We assume an initial ensemble which corresponds to such a macroscopic state that half the system is at temperature zero, while other half at temperature T . The timal evolution of this ensemble hereafter is determined purely by the law of classical dynamics. Mathematical formulation of the dynamical solution is given in section 2. The initial ensemble and the expressions of velocity-velocity correlation functions and position-position correlation functions as well as velocity-position correlation functions are given in section 3. The average kinetic and potential energies of each

15) Progress Theoret. Phys. Supplement No. 23 Part 2, (1962).

16) R. J. Rubin, *Bullet. Amer. Phys. Soc.* **II-5** 422, (1960).

17) J. Meixner, *A Model for Brownian Motion*. (Preprint, Aug. 1963).

18) S. Kashiwamura and E. Teramoto, *Progress Theoret. Phys. Supplement No. 23* 207, (1962).

19) R. E. Turner, *Physica* **26** 269, (1960).

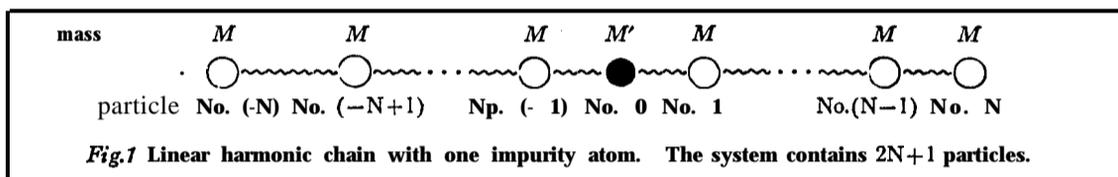
20) R. J. Rubin, *J. Math. Phys.* **1** 309, (1960); **2** 273, (1961).

21) P. Mazur and E. Montroll, *J. Math. Phys.* **1** 70, (1960).

particle in the large system are derived from these correlation functions, and their asymptotic behavior is also examined in section 4. The instantaneous heat flow is obtained from velocity-position correlation functions. It is shown that the average kinetic and potential energies of each particle in a large system approach the different stationary values in both sides of the impurity site. That is, the system approaches a *stationary* state which has a gap of the energy distribution at the impurity site. While, the heat flow still exists at every point of the system at the final state, though there is no temperature gradient at any point of the system except at the impurity site. These are given in section 5, and some discussions related to the heat flow problems in the lattice system are also given.

2. DYNAMICAL SYSTEM

We shall now consider a system of one-dimensional harmonic lattice consisting of $(2N+1)$ particles (cf. Fig. 1). Let the particles of the system be located at the integer sites numbered from $(-N)$ to $(+N)$ (from the left to the right side along the chain). They interact with two their nearest neighbours with the same harmonic constant K . They have the same mass M , except the particle of isotopic impurity of mass M' which is located at site No. 0. The displacement of the i -th particle from equilibrium position shall be written as $v_i(t)$.



Then the equations of motion read to the following:

$$\frac{d^2}{dt^2} v_i(t) = \gamma \left(1 - \frac{Q}{1+Q} \delta_{i,0} \right) \cdot \{ v_{i+1}(t) - 2v_i(t) + v_{i-1}(t) \}, \quad (1)$$

where

$$\gamma = \frac{K}{M}, \quad Q = \frac{M'}{M} - 1, \quad (2)$$

and t =time.

By introducing the Schrödinger coordinates⁽¹⁾⁽²⁾⁽¹³⁾⁽¹⁴⁾⁽²²⁾ defined by

$$\left. \begin{aligned} y_{2i} &= \frac{v_i}{\sigma\omega}, \\ y_{2i+1} &= \frac{v_{i+1} - v_i}{\sigma}, \\ \tau &= 2\omega t, \\ \omega &= \sqrt{\gamma} = \sqrt{\frac{K}{M}}, \end{aligned} \right\} \quad (3)$$

and

where σ is a reference length of the system which can be taken as unity here, and $\dot{v}_i = dv_i/dt$ is the velocity of the i -th particle; we can write the equations (1) as follows:

$$2 \frac{d}{d\tau} y_n(\tau) = \left(1 - \frac{Q}{1+Q} \delta_{n,0} \right) \cdot \{ y_{n+1}(\tau) - y_{n-1}(\tau) \}, \quad (4)$$

²²⁾ A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* p. 43, (Academic Press, New York, 1963).

for any integers n .

Now let us consider to solve equations (1) for the infinitely extended system of the chain.

Putting

$$F_{(z;\tau)} = \sum_{k=-\infty}^{+\infty} y_k(\tau) \cdot z^k, \quad (5)$$

and applying operation: $\sum_{k=-\infty}^{+\infty} z^k$ to equations (1), we obtain at once

$$2 \frac{d}{d\tau} F_{(z;\tau)} = \left(\frac{1}{z} - z \right) \cdot F_{(z;\tau)} - 2Q \frac{d}{d\tau} y_0(\tau). \quad (6)$$

The equation (6) leads to

$$F_{(z;\tau)} = \sum_{k,\mu=-\infty}^{+\infty} z^k J_{\mu-k}(\tau) \left[y_\mu^0 - Q \int_0^\tau J_\mu(\tau^*) \frac{d}{d\tau^*} y_0(\tau^*) d\tau^* \right], \quad (7)$$

where $y_\mu^0 = y_\mu(\tau=0)$ is the initial values of $y_\mu(\tau)$.

Comparing (5) with (7), we have

$$y_k(\tau) = \sum_{\mu=-\infty}^{+\infty} J_{\mu-k}(\tau) \cdot \left[y_\mu^0 - Q \int_0^\tau J_\mu(\tau^*) \cdot \frac{d}{d\tau^*} y_0(\tau^*) d\tau^* \right]. \quad (8)$$

By partial integration and by exchanging integration and summation in (8), we obtain

$$y_k(\tau) \cdot (1 + Q\delta_{k,0}) = \sum_{\mu=-\infty}^{+\infty} y_\mu^0 J_{\mu-k}(\tau) \cdot (1 + Q\delta_{\mu,0}) + Q \int_0^\tau y_0(\tau^*) \frac{d}{d\tau^*} J_k(\tau^* - \tau) d\tau^*, \quad (9)$$

where the formula:

$$J_n(y+z) = \sum_{m=-\infty}^{+\infty} J_m(y) J_{n-m}(z),$$

is used.

We put $k=0$ in (9), and obtain

$$y_0(\tau) - \frac{Q}{1+Q} \int_0^\tau y_0(\tau^*) J_1(\tau - \tau^*) d\tau^* = \frac{1}{1+Q} \sum_{\mu=-\infty}^{+\infty} y_\mu^0 J_\mu(\tau) (1 + Q\delta_{\mu,0}). \quad (10)$$

The integral equation (10) can be solved and we have its solution as follows:

$$\begin{aligned} y_0(\tau) = & \frac{1}{1+Q} \sum_{\mu=-\infty}^{+\infty} (1 + Q\delta_{\mu,0}) y_\mu^0 \cdot \left\{ J_\mu(\tau) + \right. \\ & \left. + (-1)^\mu \sum_{i=-\infty}^{-1} \delta_{\mu,i} \cdot \sum_{n=1}^{+\infty} \left(\frac{2Q}{1+Q} \right)^n \cdot \sum_{k_i=0}^{+\infty} (-1)^{k_1+k_2+\dots+k_n} J_{|\mu|+2n+2(k_1+k_2+\dots+k_n)}(\tau) \right\}. \quad (11) \end{aligned}$$

We put (11) into (9), and obtain the final solutions $y_k(\tau)$ of the difference-differential equations (4) in the following form:

$$\begin{aligned} y_k(\tau) = & \frac{1}{1+Q\delta_{k,0}} \cdot \sum_{\mu=-\infty}^{+\infty} (1 + Q\delta_{\mu,0}) y_\mu^0 \cdot \left[J_{\mu-k}(\tau) + (-1)^{(k+1)} \sum_{i=1}^{+\infty} \delta_{k,i+i'} \sum_{i''=-\infty}^{-1} \delta_{\mu,i''} \times \right. \\ & \left. \times \frac{Q}{1+Q} \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p-1} \cdot \left\{ J_{|k-1+i'+i+2p-1}(\tau) - (-1)^{\delta_{k,0}} \cdot J_{|k+1+i'+i+2p-1}(\tau) \right\} \right], \quad (12) \end{aligned}$$

with initial values y_μ^0 of $y_\mu(\tau)$.

After some calculations, we can show that the expression (12) coincides completely with the result obtained by Kashiwamura²³⁾ which is derived by means of the trigonometric eigenfunctions (normal modes) of the dynamical system for the perfect lattice.

The method we used here to obtain (12), however, is easier to understand and simpler by far than that by means of the trigonometric eigenfunctions of the system.

In terms of solutions (12) expressed by Bessel functions, we can take explicitly into account the initial conditions of the ensemble and we can diagonalize covariance matrix²⁴⁾ in the distribution function of the canonical ensemble when we want to introduce the statistics at the initial instant of time. This is shown in the following section.

As for the finitely extended system of the chain, if it is sufficiently large, we can show, by means of asymptotic expansion of Bessel functions of large order or by the proof given by the present authors²⁵⁾, that the dynamical solutions can be approximated by the solution of the infinitely extended lattice and they are written as

$$y_k(\tau) = \frac{1}{1+Q\delta_{k,0}} \sum_{\mu} (1+Q\delta_{\mu,0}) y_{\mu}^0 \cdot \left[J_{\mu-k}(\tau) + (-1)^{(k+1)} \sum_{i=1}^{+\infty} \delta_{k,i+\mu} \sum_{i=-\infty}^{-1} \delta_{\mu,i} \cdot \frac{Q}{1+Q} \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p-1} \times \right. \\ \left. \times \left\{ J_{|k-1|+|\mu|+2p-1}(\tau) - (-1)^{\delta_{k,0}} \cdot J_{|k+1|+|\mu|+2p-1}(\tau) \right\} \right], \quad (13)$$

where the summation with regard to μ covers the extended region of the chain. The end condition of the chain (for example, both ends fixed, or both ends free, etc.) gives no essential effect to the range of summation over μ , if the lattice system is sufficiently large²⁶⁾.

3. INITIAL ENSEMBLE AND CORRELATION FUNCTIONS

Now, let us introduce an initial statistical ensemble, which corresponds to such a macroscopic state that half the system (negative site) is at temperature zero, while the other half (positive site) is at temperature T . In other words, we shall take a canonical ensemble at temperature T with probability distribution function at the initial instant of time:

$$W(a_1, a_2, a_3, \dots) = \pi_s \sqrt{\frac{\sigma^2 K}{2\pi k T}} \exp\left[-\frac{\sigma^2 K}{2\pi k T} a_s^2\right], \quad (14)$$

where k is the Boltzmann constant, and the particles at the non-positive sites are quite at rest in their equilibrium positions, i.e.

$$a_0 = a_{-1} = a_{-2} = a_{-3} = \dots = 0, \quad (15)$$

where a_s (for any integers s) represents the initial value of $y_s(\tau)$, i.e. y_s^0 .

From the expression of distribution function (14), we have the elements of the initial covariance matrix defined by

$$\langle a_m \cdot a_n \rangle_{Av} = \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} a_m a_n \cdot W(a_1, a_2, a_3, \dots) \pi_p da_p \\ = \begin{cases} \frac{kT}{\sigma^2 K} \delta_{m,n} & \text{for } m \geq 1 \text{ and } n \geq 1 \\ 0 & \text{for } m \leq 0 \text{ or } n \leq 0 \end{cases} \quad (16)$$

23) S. Kashiwamura, Progress Theoret.

Statistics p. 164,

cf.

Starting from this initial distribution (14) and (15), we can pursue the statistical behavior of the system at any later time, through the expressions (13) which obey the law of purely classical dynamics. That is to say, we can determine the probability distribution of the system at any instant of the later time by the linear transformation (13) with y_{μ}^0 replaced by a_{μ} .

The probability distribution function of our total system is seen not to approach a Gaussian distribution function of $y,(\tau)$ with diagonal covariance matrix. Accordingly our total system is seen never to approach a thermodynamic equilibrium. Therefore, we can say nothing about the time change in the macroscopic temperature in our system in its strict sense, except the temperature at the initial instant of time. In this case, however, the statistical quantities of the individual particles seem to be more significant than those of the total system. Especially, in the statistical treatment of energy transport in the lattice system, we should rather take the microscopic local temperature at any point of the system, and correlation functions between particles.

Accordingly, we shall define correlation functions of the following type:

$$C_{\alpha,\beta}(\tau) = \frac{\sigma^2 K}{2k} \cdot \langle y_{\alpha}(\tau) \cdot y_{\beta}(\tau) \rangle_{Av}, \quad (17)$$

$$\left. \begin{aligned} \Theta_{m,n}(\tau) &= C_{2m,2n}(\tau), \\ U_{m,n}(\tau) &= C_{2m+1,2n+1}(\tau), \end{aligned} \right\} \quad (18)$$

and

$$V_{m,n}(\tau) = C_{2m,2n+1}(\tau), \quad (19)$$

for any integers m and n . The expressions (18) represent the velocity-velocity correlation and the position-position correlation functions, respectively. While, the expressions (19) are the velocity-position correlation functions.

Inserting the expressions (13) into (17)~(19), we can calculate the correlation functions at any instant of time, by means of the initial correlations (16).

Now, we shall define the kinetic part $\theta(m;\tau)$ and potential part $u(m;\tau)$ of the microscopic local temperature of the m -th particle at any instant of time τ . They are written as follows:

$$\theta(m;\tau) = \Theta_{m,m}(\tau), \text{ for any integers } m \quad (20)$$

and

$$u(m;\tau) = U_{m,m}(\tau), \text{ for any integers } m \quad (21)$$

The microscopic *local temperature* $T,(\tau)$ which measures the average value of the thermal energy of the m -th particle and has a dimension of temperature, is defined by:

$$\begin{aligned} T_m(\tau) &= \theta(m;\tau) + \frac{1}{2} \{ u(m;\tau) + u(m-1;\tau) \} \\ &= \frac{\sigma^2 K}{2k} \cdot \left[\langle y_{2m}^2(\tau) \rangle_{Av} + \frac{1}{2} \left\{ \langle y_{2m+1}^2(\tau) \rangle_{Av} + \langle y_{2m-1}^2(\tau) \rangle_{Av} \right\} \right]. \end{aligned} \quad (22)$$

The calculation of (22) by means of (13) and (16)~(21) gives the time change of the distribution of thermal energy. The method of calculation is quite the same as was given by the present authors.¹⁴⁾ If we take a finitely extended system of the chain, however, we have naturally the dynamical recurrence¹⁾¹²⁾²¹⁾ of the energy distribution in the lattice. And, if we want to have some analytical results, we should sum up an infinite series²⁵⁾ of Bessel functions, when we use the Schrödinger coordinates. Here, we shall put aside the dynamical recurrence

25) E. I. Takizawa and K. Kobayasi, *Chinese Journ. Phys.* **1** 83, (1963).

(17)~(19) can be easily carried out, in the same manner as was given by the present authors.¹⁴⁾

4. CORRELATION FUNCTIONS AND ASYMPTOTIC BEHAVIOR OF THERMAL ENERGY

For a sufficiently large system, we obtain, from (16), (17), and (18),

$$\begin{aligned}
C_{m,n}(\tau) \Big/ \frac{\sigma^2 K}{2k} &= \frac{kT}{\sigma^2 K} \cdot \frac{1}{(1+Q\delta_{m,0})(1+Q\delta_{n,0})} \cdot \sum_{\nu=1}^{+\infty} [J_{\nu-m}(\tau)J_{\nu-n}(\tau) + \\
&+ (-1)^{(n+1)} \sum_{i=1}^{+\infty} \delta_{n,i} \cdot \frac{Q}{Q+1} \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1}\right)^{p-1} \cdot J_{\nu-m}(\tau) \left\{ J_{\nu+n-1+2p-1}(\tau) - (-1)^{\delta_{n,0}} \cdot J_{\nu+n+1+2p-1}(\tau) \right\} + \\
&+ (-1)^{(m+1)} \sum_{i=1}^{+\infty} \delta_{m,i} \cdot \frac{Q}{Q+1} \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1}\right)^{p-1} \cdot J_{\nu-n}(\tau) \left\{ J_{\nu+m-1+2p-1}(\tau) - (-1)^{\delta_{m,0}} \cdot J_{\nu+m+1+2p-1}(\tau) \right\} + \\
&+ (-1)^{(m+1)} \sum_{i=1}^{+\infty} \delta_{m,i} + (n+1) \sum_{i=1}^{+\infty} \delta_{n,i} \cdot \left(\frac{Q}{Q+1}\right)^2 \cdot \sum_{p,q=1}^{+\infty} \left(\frac{Q-1}{Q+1}\right)^{p+q-2} \cdot \left\{ J_{\nu+m-1+2p-1}(\tau) J_{\nu+n-1+2q-1}(\tau) - \right. \\
&- (-1)^{\delta_{m,0}} \cdot J_{\nu+m+1+2p-1}(\tau) J_{\nu+n-1+2q-1}(\tau) - (-1)^{\delta_{n,0}} \cdot J_{\nu+m-1+2p-1}(\tau) J_{\nu+n+1+2q-1}(\tau) + \\
&\left. + (-1)^{\delta_{m,0} + \delta_{n,0}} \cdot J_{\nu+m+1+2p-1}(\tau) J_{\nu+n+1+2q-1}(\tau) \right\} \Big] \quad (23)
\end{aligned}$$

and

$$\begin{aligned}
C_{n,n}(\tau) \Big/ \frac{\sigma^2 K}{2k} &= \langle J_n^2(\tau) \rangle_{Av} \\
&= \frac{kT}{\sigma^2 K} \cdot \frac{1}{(1+Q\delta_{n,0})^2} \cdot \sum_{\nu=1}^{+\infty} \left[J_{\nu-n}^2(\tau) + \left(\frac{Q}{Q+1}\right)^2 \cdot \sum_{p,q=1}^{+\infty} \left(\frac{Q-1}{Q+1}\right)^{p+q-2} \cdot \left\{ J_{\nu+n-1+2p-1}(\tau) J_{\nu+n-1+2q-1}(\tau) - \right. \right. \\
&- 2(-1)^{\delta_{n,0}} \cdot J_{\nu+n-1+2q-1}(\tau) J_{\nu+n+1+2p-1}(\tau) + J_{\nu+n+1+2p-1}(\tau) J_{\nu+n+1+2q-1}(\tau) \left. \right\} + \\
&+ (-1)^{(n+1)} \sum_{i=1}^{+\infty} \delta_{n,i} \cdot \frac{2Q}{Q+1} \cdot J_{\nu-n}(\tau) \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1}\right)^{p-1} \cdot \left\{ J_{\nu+n-1+2p-1}(\tau) - \right. \\
&\left. - (-1)^{\delta_{n,0}} \cdot J_{\nu+n+1+2p-1}(\tau) \right\} \Big] \quad (23')
\end{aligned}$$

for any integers m and n .

Accordingly, from (23') we have

$$\frac{\theta(m;\tau)}{T} = C_{2m,2m} = \frac{1}{2(1+Q\delta_{m,0})} \sum_{\nu=1}^{+\infty} [\text{Bracket expression in the right hand side of (23), } n \text{ being replaced by } 2m], \quad (24)$$

$$\frac{u(m;\tau)}{T} = C_{2m+1,2m+1} = \frac{1}{2} \sum_{\nu=1}^{+\infty} [\text{Bracket expression in the right hand side of (23'), } n \text{ being replaced by } (2m+1)], \quad (25)$$

for any integers m .

For any particle at the negative site, No. $(-s)$ for $s \geq 1$,

$$\begin{aligned}
\theta(-s;\tau) = & T \cdot \sum_{\nu=1}^{+\infty} \left[J_{2s+\nu}^2(\tau) + \left(\frac{Q}{Q+1} \right)^2 \cdot \sum_{p,q=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p+q-2} \cdot \left\{ J_{2s+\nu+2p}(\tau) J_{2s+\nu+2q}(\tau) - \right. \\
& - 2J_{2s+\nu+2q}(\tau) J_{2s+\nu+2p-2}(\tau) + J_{2s+\nu+2p-2}(\tau) J_{2s+\nu+2q-2}(\tau) \left. \right\} + \\
& \left. \frac{2Q}{Q+1} \cdot J_{2s+\nu}(\tau) \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p-1} \cdot \left\{ J_{2s+\nu+2p}(\tau) - J_{2s+\nu+2p-2}(\tau) \right\} \right], \quad (26)
\end{aligned}$$

and

$$\begin{aligned}
u(-s;\tau) = & T \cdot \sum_{\nu=1}^{+\infty} \left[J_{2s+\nu-1}^2(\tau) + \left(\frac{Q}{Q+1} \right)^2 \cdot \sum_{p,q=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p+q-2} \cdot \left\{ J_{2s-1+\nu+2p}(\tau) J_{2s-1+\nu+2q}(\tau) - \right. \\
& - 2J_{2s-1+\nu+2q}(\tau) J_{2s-1+\nu+2p-2}(\tau) + J_{2s-1+\nu+2p-2}(\tau) J_{2s-1+\nu+2q-2}(\tau) \left. \right\} + \\
& \left. + \frac{2Q}{Q+1} \cdot J_{2s+\nu-1}(\tau) \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p-1} \cdot \left\{ J_{2s-1+\nu+2p}(\tau) - J_{2s-1+\nu+2p-2}(\tau) \right\} \right]. \quad (27)
\end{aligned}$$

For any particle at the positive site, No. s for $s \geq 1$,

$$\begin{aligned}
\theta(s;\tau) = & T \cdot \sum_{\nu=1}^{+\infty} \left[J_{-2s+\nu}^2(\tau) + \left(\frac{Q}{Q+1} \right)^2 \cdot \sum_{p,q=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p+q-2} \cdot \left\{ J_{2s+\nu+2p-2}(\tau) J_{2s+\nu+2q-2}(\tau) - \right. \\
& - 2J_{2s+\nu+2q-2}(\tau) J_{2s+\nu+2p}(\tau) + J_{2s+\nu+2p}(\tau) J_{2s+\nu+2q}(\tau) \left. \right\} + \\
& \left. + \frac{2Q}{Q+1} \cdot J_{-2s+\nu}(\tau) \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p-1} \cdot \left\{ J_{2s+\nu+2p}(\tau) - J_{2s+\nu+2p-2}(\tau) \right\} \right], \quad (28)
\end{aligned}$$

and

$$\begin{aligned}
u(s;\tau) = & T \cdot \sum_{\nu=1}^{+\infty} \left[J_{-2s+\nu-1}^2(\tau) + \left(\frac{Q}{Q+1} \right)^2 \cdot \sum_{p,q=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p+q-2} \cdot \left\{ J_{2s+\nu+2p-1}(\tau) J_{2s+\nu+2q-1}(\tau) - \right. \\
& - 2J_{2s+\nu+2q-1}(\tau) J_{2s+1+\nu+2p}(\tau) + J_{2s+1+\nu+2p}(\tau) J_{2s+1+\nu+2q}(\tau) \left. \right\} - \\
& \left. - \frac{2Q}{Q+1} \cdot J_{-2s+\nu-1}(\tau) \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p-1} \cdot \left\{ J_{2s+1+\nu+2p}(\tau) - J_{2s+\nu+2p-1}(\tau) \right\} \right]. \quad (19)
\end{aligned}$$

For the particle at site No. 0,

$$\begin{aligned}
\theta(0;\tau) = & \frac{T}{(1+Q)^2} \cdot \sum_{\nu=1}^{+\infty} \left[J_{\nu}^2(\tau) + 4 \left(\frac{Q}{Q+1} \right)^2 \cdot \sum_{p,q=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p+q-2} \cdot J_{\nu+2p}(\tau) J_{\nu+2q}(\tau) + \right. \\
& \left. + \frac{4Q}{Q+1} \cdot J_{\nu}(\tau) \cdot \sum_{p=1}^{+\infty} \left(\frac{Q-1}{Q+1} \right)^{p-1} \cdot J_{\nu+2p}(\tau) \right]. \quad (30)
\end{aligned}$$

It is well known that the expressions in the two cases of the heavy and the light isotopic impurity have essentially different asymptotic behaviors when τ goes to infinity. So, we should consider these two cases separately, namely for $Q > 0$ and for $-1 < Q < 0$.

When we have a heavy isotopic impurity (*i.e.* $Q > 0$) at site No. 0, we can proceed easily by means of the expressions (26)~(30). While in the case of a light isotopic impurity (*i.e.* $-1 < Q < 0$), we should rather take the solutions of equations of motion (4) in periodic expressions with regard to time τ , so that we can take explicitly into account the localized vibration in our lattice system. Here in the present paper, we shall take the case: $Q > 0$, and discuss the

asymptotic behavior of the microscopic thermal energy.

Case of a Heavy Isotopic Impurity

The mass M' of the isotopic impurity particle at site No. \bullet is greater than the mass M of other particles, i.e. $Q > 0$. In this case, we can make use of the following formulae (31) and (32) in the calculation of (26)~(30).

$$\begin{aligned} \sum_{\nu=1}^{+\infty} J_{\nu+\alpha}(\tau) J_{\nu+\beta}(\tau) &= \frac{2}{\pi} \int_0^{\frac{\pi}{2}} \sum_{\nu=1}^{+\infty} J_{2\nu+\alpha+\beta}(2\tau \cos\theta) \cos(\alpha-\beta)\theta \, d\theta \\ &= \begin{cases} \frac{2}{\pi} \int_0^{\frac{\pi}{2}} \left\{ \sum_{\nu=1}^{+\infty} J_{2\nu}(2\tau \cos\theta) - \sum_{\nu=1}^{\frac{\alpha+\beta}{2}} J_{2\nu}(2\tau \cos\theta) \right\} \cos(\alpha-\beta)\theta \, d\theta, & \text{for } \frac{\alpha+\beta}{2} \geq 1 \\ \frac{2}{\pi} \int_0^{\frac{\pi}{2}} \sum_{\nu=1}^{+\infty} J_{2\nu}(2\tau \cos\theta) \cos 2\alpha\theta \, d\theta, & \text{for } \frac{\alpha+\beta}{2} = 0 \\ \frac{2}{\pi} \int_0^{\frac{\pi}{2}} \left\{ \sum_{\nu=1}^{+\infty} J_{2\nu}(2\tau \cos\theta) + \sum_{\nu=0}^{\left|1+\frac{\alpha+\beta}{2}\right|} J_{2\nu}(2\tau \cos\theta) \right\} \cos(\alpha-\beta)\theta \, d\theta, & \text{for } \frac{\alpha+\beta}{2} \leq -1 \end{cases} \\ &= \begin{cases} -\frac{1}{\pi} \int_0^{\frac{\pi}{2}} \left\{ J_0(2\tau \cos\theta) + 2 \sum_{\nu=1}^{\frac{\alpha+\alpha}{2}} J_{2\nu}(2\tau \cos\theta) \right\} \cos(\alpha-\beta)\theta \, d\theta, & \text{for } \frac{\alpha+\beta}{2} \geq 1 \\ -\frac{1}{\pi} \int_0^{\frac{\pi}{2}} J_0(2\tau \cos\theta) \cos 2\alpha\theta \, d\theta, & \frac{\alpha+\beta}{2} = 0 \\ -\frac{1}{\pi} \int_0^{\frac{\pi}{2}} \left\{ J_0(2\tau \cos\theta) - 2 \sum_{\nu=0}^{\left|1+\frac{\alpha+\beta}{2}\right|} J_{2\nu}(2\tau \cos\theta) \right\} \cos(\alpha-\beta)\theta \, d\theta, & \text{for } \frac{\alpha+\beta}{2} \leq -1 \end{cases} \quad (31) \end{aligned}$$

for $\alpha+\beta$ =(even integers) and $\alpha-\beta \neq 0$
and

$$\sum_{\nu=1}^{+\infty} J_{\nu+\alpha}^2(\tau) = \begin{cases} \frac{1}{2} \left\{ 1 - J_0^2(\tau) \right\} - \sum_{\nu=1}^{\alpha-1} J_{\nu}^2(\tau), & \text{for } \alpha \geq 1 \\ \frac{1}{2} \left\{ 1 - J_0^2(\tau) \right\}, & \text{for } \alpha = 0 \\ \frac{1}{2} \left\{ 1 - J_0^2(\tau) \right\} + \sum_{\nu=0}^{|\alpha|} J_{\nu}^2(\tau), & \text{for } \alpha \leq -1 \end{cases} \quad (32)$$

for any integers α and β .

The microscopic local temperatures defined by equation (22) approach the same stationary value $T/2$ in a large system of perfect lattice^{12,13,14}, when τ goes to infinity. Here, the asymptotic behavior of (22) in the limit: $\tau \rightarrow +\infty$, shall be examined in our system with an impurity particle. In calculating the effect of an impurity to the microscopic local temperature, we use the following formula¹⁴):

$$\lim_{\tau \rightarrow +\infty} \sum_{\mu=1}^{+\infty} J_{\mu+\alpha}(\tau) J_{\mu-\beta}(\tau) = \lim_{\tau \rightarrow +\infty} \frac{1}{\pi} \int_0^{\frac{\pi}{2}} d\theta \cdot \cos(2\alpha\theta) \cdot \int_0^{2\tau \cos\theta} d\xi \cdot J(\xi)$$

$$\begin{aligned}
&= \frac{1}{\pi} \int_0^{\frac{\pi}{2}} d\theta \cdot \cos(2\alpha\theta) \int_0^{\infty} d\xi \cdot J_1(\xi) \\
&= \frac{1}{\pi} \int_0^{\frac{\pi}{2}} d\theta \cdot \cos(2\alpha\theta) = \frac{(-)^{\alpha}}{2\pi\alpha}, \quad \text{for any integers } \alpha
\end{aligned}$$

in the expressions (26)~(30).

The results obtained here (33) and (34) can be shown essentially the same as those obtained by Kashiwamura and Teramoto. It should be mentioned, however, that the method we used here is easier to calculate and simpler by far than theirs by means of the trigonometric functions.

It is found that

for $Q \geq 0$,

$$\left. \begin{aligned}
\lim_{\tau \leftarrow +\infty} \theta(n; \tau) &= \frac{1+2Q}{4(1+Q)} T, \\
\lim_{\tau \rightarrow +\infty} \theta(-n; \tau) &= \frac{1}{4(1+Q)} T, \\
\lim_{\tau \rightarrow +\infty} u(n; \tau) &= \frac{1+2Q}{4(1+Q)} T, \\
\lim_{\tau \rightarrow +\infty} u(-n; \tau) &= \frac{1}{4(1+Q)} T, \\
\lim_{\tau \rightarrow +\infty} \theta(0; \tau) &= \frac{1}{4(1+Q)} T,
\end{aligned} \right\} \quad (33)$$

for any positive integers n , and

for $n=0$.

Accordingly, from (33) we see that the microscopic local temperatures (22) which have the initial value T at the positive sites, and zero at the negative sites, approach the stationary values, as follows:

For $Q \geq 0$,

$$\left. \begin{aligned}
\lim_{\tau \rightarrow +\infty} T_n(\tau) &= \frac{1+2Q}{2(1+Q)} T, \\
\lim_{\tau \rightarrow +\infty} T_0(\tau) &= \frac{2+Q}{4(1+Q)} T, \\
\lim_{\tau \rightarrow +\infty} T_{-n}(\tau) &= \frac{1}{2(1+Q)} T,
\end{aligned} \right\} \quad (34)$$

and

for any positive integers n .

From (34), we can see that the completely uniform distribution of energy along the system of the lattice can not be attained at $\tau = +\infty$. The microscopic temperatures in positive sites and in negative sites approach the different stationary values, remaining a gap of the energy distribution at the impurity site. The height of the gap of the microscopic local temperature at the impurity site is

$$\frac{|Q|}{1+|Q|} T. \quad (35)$$

The expression (35) has a limiting value T as Q goes to infinity, which corresponds to the

case of infinite mass of the impurity atom ($M' \rightarrow +\infty$). In other words, the impurity atom plays a role of fixed wall, and prevents the flow of energy across that point. The expression (35) has also a limiting value $T/2$ as Q approaches (-1) which corresponds to $M'=0$. For a perfect lattice, *i.e.* for the case $Q=0$, the stationary state in the system with uniform microscopic local temperatures:

$$\lim_{\tau \rightarrow +\infty} T_n(\tau) = \frac{1}{2} T, \quad (36)$$

for any integers n , is established⁽¹²⁾⁽¹³⁾⁽¹⁴⁾ as we expect.

5. FLOW OF ENERGY IN THE SYSTEM

The asymptotic behavior of the kinetic and potential energies in (33) is expressed by (34) and we found that the microscopic local temperatures approach stationary values at the final state: $\tau = +\infty$. This result, however, does not mean that our system approach the thermodynamic equilibrium at $\tau = +\infty$. In fact, the correlation matrix $\|V_{m,n}(\tau)\|$ in (19) of our ensemble has nonvanishing elements at the final state: $\tau = +\infty$, and we can show that the energy flow still exists at every point of the system even at $\tau = +\infty$.

The energy flow from the n -th particle to the $(n-1)$ -th particle can be given by the rate of change of total energy contained in the system of particles in the positive side (in the right-hand side) of the n -th particle. Let us write the total energy in the positive side of the n -th particle by $E_n(\tau)$. Then we obtain

$$E_n(\tau) = \sum_{s=n}^{+\infty} \left\{ \frac{1}{2} M(1+Q\delta_{s,0}) \dot{v}_s^2 + \frac{1}{2} K(v_{s+1} - v_s)^2 \right\}. \quad (37)$$

Accordingly, we obtain, by means of (4),

$$\begin{aligned} -\frac{dE_n(\tau)}{d\tau} = & -\frac{\sigma^2 K}{2} \cdot \sum_{s=n}^{+\infty} \left[(1+Q\delta_{s,0}) \left(1 - \frac{Q}{1+Q} \delta_{s,0} \right) \cdot y_{2s}(y_{2s+1} - y_{2s-1}) + \right. \\ & \left. + y_{2s+1}(y_{2s+2} - y_{2s}) \right], \end{aligned} \quad (38)$$

which takes a little different expressions as to whether the summation covers $s=0$ (impurity site) or not.

If we take $n=0$ in (38), then we obtain

$$-\frac{dE_0(\tau)}{d\tau} = \frac{\sigma^2 K}{2} \cdot y_0(\tau) y_{-1}(\tau), \quad (39)$$

which corresponds to the energy flow from the right-hand side of the zero-th particle to the left-hand side of the (-1) -th particle, and corresponds physically to the work done by the zero-th particle upon the (-1) -th particle.

Calculating the average value of (39), we obtain from (19),

$$\left\langle -\frac{dE_0(\tau)}{d\tau} \right\rangle_{Av} = k \cdot C_{0,-1}(\tau) \quad (40)$$

We can calculate the correlation matrix $\|V_{m,n}(\tau)\|$ as function of time, and we take the limit: $\tau \rightarrow +\infty$. Then the expression (40) for positive Q , becomes:

$$\lim_{\tau \rightarrow +\infty} \left\langle -\frac{dE_0(\tau)}{d\tau} \right\rangle_{Av} = \left. \begin{array}{l} \frac{kT}{2\pi(1+Q)^2} \left\{ \frac{1+Q}{1-Q} - \frac{Q^2(1+Q)}{1+Q(1-Q)} \right\}^{1/2} \log \frac{1+\sqrt{1-Q^2}}{Q}, \text{ for } 0 < Q < 1 \\ \frac{kT}{3\pi}, \text{ for } Q=1 \\ \frac{kT}{2\pi(1+Q)^2} \left\{ \frac{4Q^2}{(1+Q)^2} \left(\frac{Q+1}{Q-1} \right)^{3/2} \cdot \operatorname{arctg} \left(\frac{Q-1}{Q+1} \right)^{1/2} + \right. \\ \quad \left. + \frac{Q^2}{\sqrt{Q^2-1}} \operatorname{arctg} \sqrt{Q^2-1} - \frac{Q+1}{Q-1} \right\}, \text{ for } 1 < Q \\ \frac{kT}{2\pi} \text{ for } Q=0 \end{array} \right\} \quad (41)$$

It is worth while remarking that our results have very similar qualitative properties to the change of temperature in a perfect lattice¹²⁾¹³⁾¹⁴⁾. We can also compare the flow of energy in our system containing an impurity atom, with the heat flow in an infinite rod. In our system, however, Fourier's law which states that the vector of heat flow is proportional to the gradient of temperature, does not hold at every point of the system, even at $\tau = +\infty$. We have known¹⁴⁾ and also we can derive from our present results that even in perfect lattice ($M' = M$) of infinite length, there exists a constant energy flow $kT\omega/\pi$ at every point throughout the system, though the whole system attains uniform distribution of microscopic local temperature $T/2$ at $\tau = +\infty$. Also in our present system, the constant flow of energy exists throughout the system from the right side to the left side at the final state: $\tau = +\infty$. While the uniform local temperature is attained in both sides of the impurity atom. In this respect, the energy flow in the harmonic lattice is essentially different¹²⁾¹³⁾¹⁴⁾ from the heat flow in a classical system.

From our present results, we could also interpret the effect of many number of isotopic impurity atoms in a one-dimensional or in a three-dimensional lattice. We can also expect the existence of stationary values of the microscopic local temperatures in the onedimensional and in the three-dimensional cases. We can also expect the existence of gaps of energy distribution at the impurity sites and the existence of the energy flow which does not obey the classical Fourier's law.

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