Non-Clausius heat transfer: the example of harmonic chain with an impurity

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Received 4 September 2019
Accepted for publication 11 March 2020
Published 24 June 2020

Online at stacks.iop.org/JSTAT/2020/063212
https://doi.org/10.1088/1742-5468/ab837c

Abstract. Motivated by recent discussion about the possibility of non-Clausius (from cold to hot) heat flow, we revisit the familiar model of an impurity atom of mass $M$ embedded in an otherwise uniform one-dimensional harmonic lattice of host atoms of mass $m$. Assuming that the initial distributions for the impurity and the rest of the lattice are uncorrelated and have canonical forms with given temperatures, we show that the average kinetic energy of the impurity may increase with time even if its initial temperature is higher than or equal to that of the lattice. Such an increase is only temporary in uniform lattices and in lattices with a heavy impurity ($M \geq m$), but may be permanent in lattices with a localized vibrational mode generated by a light impurity ($M < m$). Thus the model shows a non-Clausius spontaneous heat transfer directed from a colder lattice to a hotter impurity.

Keywords: fluctuation phenomena, stochastic thermodynamics, transport processes/heat transfer
1. Introduction

According to the Clausius formulation of the second law of thermodynamics, heat cannot spontaneously flow from a colder system to a hotter one. It is often tacitly implied that this statement concerns only macroscopic systems. The question of whether the statement holds at the micro scale has received some attention in recent years, in particular as a part of a more general renewed debate about the statistical definition of entropy (Boltzmann’s versus Gibbs’) and the consistency of the negative temperature concept [1–8].

For isolated systems described by the micro canonical ensemble, a primary state variable is not temperature but internal energy. On this premise, it was argued that the sign of the temperature difference alone does not necessarily determine the direction of heat flow when two initially isolated systems are brought into contact; it is thus anticipated that under certain conditions heat can flow from cold to hot [1, 3, 4, 9]. We shall call such anomalously directed heat transfer non-Clausius. Other authors have disputed the possibility of non-Clausius heat flow and criticized the thermodynamic arguments in support of it; see [8] and references therein.

Motivated by this discussion, in this paper we revisit the familiar model of an impurity atom, or isotope, embedded in a one-dimensional harmonic lattice. The model is entirely dynamical, except that the initial conditions for the impurity and the rest of the lattice are given by the canonical distributions with given (in general, different)
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Temperatures. We show that the initially hotter isotope may get energy from the colder lattice and, in the case of a light isotope, permanently keep that energy. Thus the terse version of the Clausius statement (heat cannot spontaneously flow from cold to hot) may be violated at the level of microscopic dynamics. On the other hand, using a setting discussed in the paper, one apparently cannot design a cyclic process to transfer heat from a cold system to a hot one in a systematic way; therefore the second law is not violated.

Technically, our discussion is based on a generalized Langevin equation for the impurity atom. For the setting when the impurity and lattice are statistically uncorrelated and have different initial temperatures, the Langevin equation involves an additional force known as the initial slip, which depends on the impurity’s initial condition. The initial slip often produces only transient, though possibly long-lived, effects [10–13]. On the other hand, in an isolated lattice with localized vibrational modes [18–24] the initial slip is expected to be essential at all times. We demonstrate that the initial slip may be responsible for a non-Clausius heat transfer. The properties of the latter strongly depend on whether the impurity generates a localized vibrational mode and correlate with the ergodic properties of the model.

2. Model

Consider a one-dimensional lattice of $2N + 1$ atoms, labeled from $-N$ to $N$, connected by identical linear springs with the force constant $k$, see figure 1. All atoms except the central one have the same mass $m$, the central atom is an isotope with the mass $M$. The key parameter is the mass ratio

$$\alpha = \frac{m}{M},$$

(1)

which determines the dynamical and ergodic properties of the model. We shall assume that the lattice is infinitely large, $N \to \infty$, in which case a specific choice of boundary conditions is immaterial. To be specific, we shall assume that the terminal atoms are attached to infinitely heavy walls by the springs with the same force constant $k$ as for the bulk of the lattice, see figure 1. The model is well familiar, but it is often discussed in the statistical mechanics literature under the assumption that the whole lattice is initially in thermal equilibrium, or that the uniform part of the lattice is initially equilibrated in the field of the isotope fixed at a given initial position. Here we wish to adopt the initial condition of different kind, namely when the isotope and the rest of the lattice are initially equilibrated independently at different temperatures.

Let us write the Hamiltonian of the lattice as a sum of three terms

$$H = H_s + H_b + H_c,$$

(2)

The term $H_s$ involves only the coordinate $Q$ and momentum $P$ of the isotope,

$$H_s = \frac{P^2}{2M} + kQ^2.$$  

(3)

We shall refer to the isotope as the system (of interest), using the terms ‘isotope’ and ‘system’ interchangeably. The term $H_b$ involves coordinates $\{q_i\}$ and momenta $\{p_i\}$ of all
Figure 1. The lattice at times $t < 0$: the central isotope (black circle) is fixed in the mechanical equilibrium position, as denoted by the symbol ▲; other atoms (white circles), referred to as the bath, are coupled to an external thermal reservoir (depicted as a rectangle below the lattice) of temperature $T$. At $t = 0$ the connection to the external reservoir and the constraint ▲ are removed, and the lattice begins to evolve as an isolated system. Initial conditions for the bath atoms are given by the canonical distribution (8) with temperature $T$. The initial condition for the isotope is chosen to be described by the canonical distribution (9) with the effective temperature $T_0$.

other atoms of the lattice, which we shall refer to as the bath. We write the Hamiltonian of the bath as a sum of two parts corresponding to the right and left parts of the lattice

$$H_b = H_r + H_l,$$

$$H_r = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{k}{2} \left\{ q_1^2 + (q_2 - q_1)^2 + \cdots + (q_N - q_{N-1})^2 + q_N^2 \right\},$$

$$H_l = \sum_{i=-1}^{-N} \frac{p_i^2}{2m} + \frac{k}{2} \left\{ q_1^2 + (q_2 - q_1)^2 + \cdots + (q_N - q_{N+1})^2 + q_{-N}^2 \right\}.$$ (6)

The term $H_c$ describes bilinear coupling of the system and the bath,

$$H_c = -k(q_1 + q_{-1})Q.$$ (7)

As usual, the coordinates $\{q_i\}$ and $Q$ are identified with displacements of atoms from their mechanical equilibrium positions.

The initial condition is defined as follows. We assume that at times $t < 0$ the isotope, or the system, is fixed in its mechanical equilibrium position $Q = 0$, while the rest of the lattice (the bath) is in thermal equilibrium with an external thermal reservoir with temperatures $T$, see figure 1. The state of the lattice at $t < 0$ can be characterized as a state of constrained equilibrium to emphasize that an external constraint (denoted in figure 1 by the symbol ▲) is applied to fix the initial position of the system. At $t = 0$ the contact with the external thermal reservoir and the constraint fixing the system’s position are removed, and for $t > 0$ the lattice evolves as an isolated one.

The initial distribution for the bath $\rho_b$ is determined by the previous contact with the external reservoir with temperature $T$ and therefore has the canonical form,

$$\rho_b = c e^{-H_b/T}. $$ (8)
Here and throughout the paper we express temperature in energy units, i.e. multiplied by Boltzmann’s constant $k_B$. The initial distribution for the system $\rho_s$ we chose to be of the canonical form

$$\rho_s = c e^{-H_s/T_0}$$

with Hamiltonian $H_s$ given by (3) and the parameter $T_0$ playing the role of the isotope’s initial temperature. Such initial condition can be characterized as a sudden preparation [12] in the sense that the bath has no time to adjust to initial parameters of the system. One may interpret the initial distribution (9) as follows: immediately after it is released at $t = 0$, the isotope is harmonically trapped in the potential $kQ^2$ and reaches thermal equilibrium with an external thermal reservoir with temperature $T_0$ on a timescale much shorter than any other characteristic times of the problem. Note that Hamiltonian $H_s$ in (9) depends on the coordinate and momentum of the system only, and does not involve interaction with the bath. This reflects our assumption that the system and bath are initially thermalized independently.

Already at this stage of the discussion, one may anticipate that the model may show properties which are unusual from the point of view of macroscopic thermo statistics. Even if the initial temperatures of the system and the bath are the same, $T_0 = T$, the overall lattice at $t = 0$ is not in thermal equilibrium. Indeed, the initial distribution $\rho_s \rho_b \sim e^{-(H_s+H_b)/T}$ does not involve the coupling Hamiltonian $H_c$, and therefore is not the equilibrium distribution $\rho_e \sim e^{-H/T} = e^{-(H_s+H_b+H_c)/T}$ for the lattice. This feature is not a surprise, considering that in macroscopic thermo statistics the interaction energy of the system and the bath is assumed to be negligible compared to the internal energy of the system. On the other hand, for microscopic systems strongly coupled to the environment the interaction energy is not negligible, and one may anticipate a transient heat flow between the system and bath even if their temperatures are the same.

### 3. Langevin equation

The dynamics of the model described in the previous section can be analyzed in many ways; here we use the method based on a microscopically derived Langevin equation for the isotope. Integrating equation of motion for the bath atoms, substituting the results into the equation of motion for the isotope, and taking the limit of the infinite lattice $N \to \infty$, one derives for the isotope’s momentum the following generalized Langevin equation:

$$\dot{P}(t) = -\int_0^t K(t-\tau) P(\tau) d\tau + \xi(t) - MQ(0)K(t).$$

This equation has been the subject of many works, see e.g. [12–14]. In order to make the paper self-contained we provide the derivation in appendix A. In equation (10), the term $\xi(t)$ is a stochastic force which for the present model is available as an explicit linear function of initial coordinates and momenta of the bath $\{q_i, p_i\}$, see equation (A19). One can show that $\xi(t)$ is a zero-centered and stationary process related to the memory
kernel $K(t)$ by the standard fluctuation-dissipation relation,
\[ \langle \xi(t) \rangle = 0, \quad \langle \xi(t) \xi(t') \rangle = MTK(t - t'). \] (11)
Here the average is taken over initial coordinates and momenta of the bath $\{q_i, p_i\}$ with the distribution $\rho_b$ given by equation (8). Let us note that although properties (11) for $\xi(t)$ are standard, they should not be taken for granted. In general, when the bath initially is not in equilibrium with the system, as in our model, the stochastic force $\xi(t)$ may have more complicated properties [15].

The memory kernel $K(t)$ in equation (10) for the infinite lattice is known to have the form
\[ K(t) = \frac{\alpha \omega_0}{t} J_1(\omega_0 t) = \frac{\alpha \omega_0^2}{2} \left\{ J_0(\omega_0 t) + J_2(\omega_0 t) \right\}, \] (12)
where $J_n(x)$ are Bessel functions, $\alpha = m/M$ and $\omega_0 = 2\sqrt{k/m}$, see appendix A. We shall also need the Laplace transform $\tilde{K}(s) = \int_0^\infty e^{-st}K(t)dt$ of kernel (12), which reads
\[ \tilde{K}(s) = \frac{\alpha \omega_0^2}{s + \sqrt{s^2 + \omega_0^2}} = \alpha \left( -s + \sqrt{s^2 + \omega_0^2} \right). \] (13)

A distinctive feature of the Langevin equation (10) is the force $-MQ(0)\dot{K}(t)$, known as the initial slip [10–13], which is a linear function of the isotope’s initial displacement $Q(0)$. The initial slip vanishes for the initial condition $Q(0) = 0$, but it does not appear in the Langevin equation also for special initial distributions with $Q(0) \neq 0$. In particular, if initial values of the bath variables are drawn from the distribution
\[ \rho_c = c e^{-[H_b+H_s]/T} \] (14)
then the initial slip has to be absorbed in the stochastic force $\xi(t)$ in order to make the latter zero-centered [14, 16]. Distribution (14), which is often exploited in microscopical models of open systems at strong coupling (see, e.g., references [17, 26]), implies that the bath at $t = 0$ is in equilibrium with the system fixed at a given position. This assumes that the bath variables are fast and quickly adjust (reach equilibrium with) the slowly moving system. In this paper we keep in mind a quite different physical situation when the system and bath at $t < 0$ do not interact and are individually equilibrated to canonical states with different temperatures. Respectively, instead of using distribution (14) we assume that initial states of the bath and system are not correlated and described by canonical distributions $\rho_b$ and $\rho_s$, given by equations (8) and (9). In that case the initial slip in the Langevin equation (10) does not vanish and will be shown to play an important role.

4. Thermalization and non-thermalization

Solving the Langevin equation (10) with the Laplace transform method one gets
\[ P(t) = P(0)R(t) + \int_0^t R(\tau)\xi(t - \tau)d\tau + MQ(0)\dot{R}(t), \] (15)
where the dimensionless function $R(t)$ has the Laplace transform

$$\tilde{R}(s) = \frac{1}{s + K(s)}.$$  

(16)

In the time domain $R(t)$ satisfies the following equation and initial condition:

$$\dot{R}(t) = -\int_0^t K(t - \tau)R(\tau)d\tau, \quad R(0) = 1.$$  

(17)

We shall call the function $R(t)$ the resolvent. As follows from the above relations, the resolvent $R(t)$ is a solution of the generalized Langevin equation (10) for the special initial condition when $P(0) = 1$, $Q(0) = 0$, and initial displacements and momenta of all atoms of the bath are zero, $q_i(0) = p_i(0) = 0$ for $\forall i$. Indeed, as shown in appendix A, the fluctuating force $\xi(t)$ is a linear function of initial bath variables. Then for the above mentioned initial conditions $\xi(t) = 0$ for any $t$, and equation (15) gives $P(t) = R(t)$.

The resolvent $R(t)$ is also equal to a more familiar character of statistical mechanics, namely the normalized equilibrium correlation function

$$C(t) = \frac{\langle P(0)P(t) \rangle_e}{\langle P^2 \rangle_e}.$$  

(18)

Here the average $\langle \cdots \rangle_e$ is taken over initial coordinates and momenta of the overall lattice with the canonical equilibrium distribution $\rho_e = e^{-\mathcal{H}/T}. The equality $C(t) = R(t)$ can be verified by constructing from (15) the expression for $C(t)$. Alternatively, one can notice that when the system and the bath are in equilibrium, the Langevin equation for the system has the standard form with no initial slip,

$$\dot{P}(t) = -\int_0^t K(t - \tau)P(\tau)d\tau + \xi(t),$$  

(19)

where $\xi(t)$ is zero-centered, $\langle \xi(t) \rangle_e = 0$, and uncorrelated with $P(0)$. Multiplying this equation by $P(0)$, taking the average and normalizing, one finds that $C(t)$ satisfies the initial value problem

$$\dot{C}(t) = -\int_0^t K(t - \tau)C(\tau)d\tau, \quad C(0) = 1,$$  

(20)

which is the same as equation (17) as for the resolvent. The two functions therefore are equal, $R(t) = C(t)$. An explicit expression for the equilibrium correlation function $C(t)$ for the present model is well-known [18]; we shall exploit that result identifying $C(t)$ with the resolvent $R(t)$.

Within the Langevin approach, it is natural to describe the system’s dynamics by evaluating the moments $\langle P^n(t) \rangle$. We shall focus on the first two moments, $\langle P(t) \rangle$ and $\langle P^2(t) \rangle$, taking the average $\langle \cdots \rangle$ over the initial bath variables $\{q_i(0), p_i(0)\}$ with the canonical distribution $\rho_b$ given by equation (8).

The expression for the first moment follows immediately from equation (15),

$$\langle P(t) \rangle = P(0)R(t) + MQ(0)\dot{R}(t).$$  

(21)
Squaring equation (15) and taking the average, one gets for the second moment the expression
\[
\langle P^2(t) \rangle = P^2(0)R^2(t) + \int_0^t d\tau \int_0^t d\tau' R(\tau)R(\tau')\langle \xi(\tau)\xi(\tau') \rangle + [MQ(0)\dot{R}(t)]^2 \\
+ MP(0)Q(0) \frac{d}{dt}R^2(t).
\]
(22)

Here we took advantage of the stationarity of the stochastic force, \(\langle \xi(t-\tau)\xi(t-\tau') \rangle = \langle \xi(\tau)\xi(\tau') \rangle\). The double integral over the square \([0, t] \times [0, t]\) can be written as two times the integral over a triangle,
\[
2 \int_0^t d\tau R(\tau) \int_0^\tau d\tau' R(\tau')\langle \xi(\tau)\xi(\tau') \rangle.
\]
(23)

Using the fluctuation-dissipation relation (11) and equation (17), this can be further worked out as follows:
\[
2MT \int_0^t d\tau R(\tau) \int_0^\tau d\tau' K(\tau - \tau')R(\tau') = -2MT \int_0^t d\tau R(\tau)\dot{R}(\tau) = MT \left[ 1 - R^2(t) \right].
\]
(24)

Then expression (22) takes the form
\[
\langle P^2(t) \rangle = P^2(0)R^2(t) + MT[1 - R^2(t)] + [MQ(0)\dot{R}(t)]^2 + MP(0)Q(0) \frac{d}{dt}R^2(t).
\]
(25)

As follows from (21) and (25), the ergodic properties of the model are determined by the asymptotic properties of the resolvent and its derivative: if \(R(t)\) and \(\dot{R}(t)\) both vanish in the long time limit,
\[
R(t) \to 0, \quad \dot{R}(t) \to 0, \quad \text{as} \quad t \to \infty,
\]
(26)

then the moments thermalize, i.e. evolve towards the equilibrium values,
\[
\langle P(t) \rangle \to 0, \quad \langle P^2(t) \rangle \to MT, \quad \text{as} \quad t \to \infty.
\]
(27)

For the present model thermalization is known to occur for a heavy isotope or for a uniform lattice, \(M \geq m\), or \(\alpha \leq 1\) \cite{14, 18, 22}. Even though the harmonic lattice is not an ergodic system, a heavy isotope embedded in the lattice shows the ergodic behavior. On the other hand, for a light isotope, \(M < m\), or \(\alpha > 1\) the resolvent \(R(t)\) involves a non-vanishing oscillating component known as a localized vibrational mode \cite{18–22}. In that latter case the condition (26) is not satisfied, and the light isotope does not reach thermal equilibrium with the bath.

We postpone the further discussion of ergodic properties of the model and the evaluation of the resolvent until section 6.
5. Heat transfer

Recall that expressions (21) and (25) for the moments $\langle P(t) \rangle$ and $\langle P^2(t) \rangle$ involve averaging over the bath variables only. Now we take an additional average of that expressions $\langle \cdots \rangle_s = \int dQ dP \rho_s(\cdots)$ over the initial isotope’s coordinate and momentum $Q = Q(0), P = P(0)$ with distribution $\rho_s$ given by (9),

$$\langle P(t) \rangle = \langle P \rangle_s R(t) + M \langle Q \rangle_s \dot{R}(t),$$

$$\langle P^2(t) \rangle = \langle P^2 \rangle_s R^2(t) + MT[1 - R^2(t)] + M^2 \langle Q^2 \rangle_s [\dot{R}(t)]^2 + M \langle PQ \rangle_s \frac{d}{dt} R^2(t).$$

(28)

With $H_s$ given by equation (3), the distribution $\rho_s = ce^{-H_s/T_0}$ describes the equilibrium state of a harmonic oscillator with mass $M$ and spring constant $2k$, and therefore has the moments

$$\langle P \rangle_s = \langle Q \rangle_s = \langle PQ \rangle_s = 0, \quad \langle P^2 \rangle_s = MT_0, \quad \langle Q^2 \rangle_s = \frac{1}{2k} T_0.$$

(29)

Substituting these values into equation (28), we find that the first moment vanishes, $\langle P(t) \rangle = 0$, and the second moment takes the form

$$\langle P^2(t) \rangle = MT_0 R^2(t) + MT[1 - R^2(t)] + \frac{2M}{\alpha \omega_0^2} T_0 [\dot{R}(t)]^2.$$

(30)

Here we take into account that $M/k = 4/(\alpha \omega_0^2)$. Thus, the kinetic energy of the system $E = \langle P^2 \rangle/2M$, averaged over initial variables of both the system and bath, reads

$$E(t) = \frac{T_0}{2} R^2(t) + \frac{T}{2} [1 - R^2(t)] + \frac{T_0}{\alpha \omega_0^2} [\dot{R}(t)]^2.$$

(31)

Our interest is to compare $E(t)$ with the system’s initial kinetic energy $E(0) = T_0/2$ evaluating the energy change

$$\Delta E(t) = E(t) - E(0) = E(t) - T_0/2.$$

(32)

The sign of $\Delta E(t)$ characterizes the direction of the net heat transfer during the time interval $(0, t)$: $\Delta E(t) > 0$ suggests that the system absorbs heat from the bath, while $\Delta E(t) < 0$ corresponds to the transfer of heat in the opposite direction. From (31) and (32) one obtains

$$\Delta E(t) = \frac{1}{2} [1 - R^2(t)](T - T_0) + \frac{1}{\alpha \omega_0^2} [\dot{R}(t)]^2 T_0.$$

(33)

In the following sections we shall discuss the explicit forms which the function $\Delta E(t)$ takes for the cases of heavy and light isotopes. However, some general features of the heat transfer can be observed already at this stage based only on the asymptotic properties of the resolvent.

https://doi.org/10.1088/1742-5468/ab837c
As was discussed in section 6, for a heavy isotope ($\alpha \leq 1$) the resolvent $R(t)$ and its derivative $\dot{R}(t)$ both vanish at long times. As a consequence, the dynamics of a heavy isotope is irreversible and ergodic: the isotope reaches thermal equilibrium with the lattice. From equation (33) we find that for a heavy isotope the kinetic energy change reaches the long-time asymptotic value

$$\Delta E(t) \to \frac{1}{2}(T - T_0), \quad t \to \infty,$$

(34)

which corresponds to a Clausius heat transfer from hot to cold. The same value we obtain for $\Delta E(t)$ averaged over an infinitely long time interval,

$$\bar{\Delta E} = \lim_{t \to \infty} \frac{1}{t} \int_0^t \Delta E(\tau) d\tau.$$  

(35)

Thus we find that for the present model the ergodic dynamics also implies that the net heat transfer between the system and the bath on the long time scale is Clausius.

On the other hand, one can observe from equation (33) that Clausius heat transfer is a property that should not be taken for granted. In general, it only holds for ergodic systems, and only on the asymptotically long time interval. For a non-ergodic system, like a light isotope, $R(t)$ does not vanish at long times. In that case, as we shall see in section 8, equation (33) may give a non-Clausius heat transfer. Moreover, even for the ergodic dynamics of a heavy isotope equation (33) predicts that heat transfer may be non-Clausius on a finite time interval. The first term in the right-hand side of equation (33) is proportional to the temperature difference $T - T_0$ and thus describes a Clausius net heat transfer. On the other hand, the second term in equation (33) does not involve the temperature difference, but depends on the initial temperature of the system only. Being non-negative, the second term describes a heat flow directed from the bath to the system even for $T_0 \geq T$. Then the sign of the net kinetic energy balance may depend not only on the temperature difference, but also on the relative strength of the two terms in equation (33).

Suppose $T > T_0$, i.e. the bath is hotter than the system. For any $t > 0$ in (33) the first term is positive and the second one is non-negative, so that $\Delta E(t) > 0$. Thus, for $T > T_0$ the net heat transfer is always Clausius: the colder system gets a positive amount of energy from the hotter bath. However, since the resolvent $R(t)$ is, in general, a non-monotonic function, equation (33) shows that on finite time intervals $\Delta E(t)$ may be negative.

When $T = T_0$ the first term in (33) is zero, and $\Delta E(t) \geq 0$. The heat transfer is non-Clausius: the system receives some energy from the bath despite the temperatures of the system and the bath are the same. When the system is a heavy isotope ($\alpha \leq 1$), then $\dot{R}(t) \to 0$ as $t \to \infty$, and according to (33), $\Delta E(t)$ vanishes at long times. In this case the non-Clausius heat transfer is transient and vanishes in the long time limit. On the other hand, if the system is a light isotope, $\alpha > 1$, then $\dot{R}(t)$ does not vanish but rather oscillates at long times. In this case, the time average of $\Delta E(t)$, defined by (35), is positive, $\bar{\Delta E} > 0$, and the non-Clausius heat transfer is permanent.

Now suppose $T < T_0$, i.e. the isotope is initially hotter than the bath. In this case the two terms in (33) have different signs and, as we noted above, the net heat transfer
may be either Clausius or non-Clausius depending on the relative values of the first and second terms. It is clear, however, that for a small temperature difference the first term, at least at short times, is smaller by the absolute value than the second one, so that $\Delta E(t) > 0$. This corresponds to a non-Clausius heat transfer: the initially hotter system receives energy from the colder bath. Similarly to the case $T = T_0$, the system’s energy gain is only temporary for $\alpha \leq 1$ but may be permanent for $\alpha > 1$.

For a further analysis and illustrations we need explicit expressions for the resolvent $R(t)$.

### 6. Resolvent, ergodicity, and localized modes

As discussed in the previous sections, the ergodic and heat transfer properties of the present model are governed by the asymptotic long-time properties of the resolvent $R(t)$. As follows from equations (16) and (13), the Laplace transform of the resolvent reads

$$\tilde{R}(s) = \frac{1}{\alpha \sqrt{s^2 + \omega_0^2} - (\alpha - 1)s}.$$  \hfill (36)

Recall that here $\alpha = m/M$ is the mass ratio, and $\omega_0 = 2\sqrt{k/m}$ is the maximal normal mode frequency of the uniform lattice. The inversion of (36) in closed form is possible only for a uniform lattice,

$$R(t) = J_0(\omega_0 t), \quad \text{if} \quad \alpha = 1,$$  \hfill (37)

and for a heavy isotope two times heavier than atoms of the chain,

$$R(t) = \frac{2}{\omega_0 t} J_1(\omega_0 t), \quad \text{if} \quad \alpha = 1/2,$$  \hfill (38)

where $J_n(x)$ are Bessel functions. In both cases the resolvent and its derivative vanish at long times and, according to (25), the isotope reaches thermal equilibrium with the bath. It turns out that this scenario holds also for any $\alpha \leq 1$. For that case the inversion of (36) gives the following result:

$$R(t) = \varphi(t) = \frac{2\alpha}{\pi} \int_0^{\omega_0} \frac{\sqrt{\omega_0^2 - y^2} \cos(\omega_0 t)}{(1 - 2\alpha)y^2 + \alpha^2 \omega_0^2} \, dy, \quad \text{if} \quad \alpha \leq 1.$$  \hfill (39)

One can verify that the function $\varphi(t)$ given by this expression decays to zero at long times for any $\alpha$. For $\alpha = 1$ and $\alpha = 1/2$ expression (39) is reduced to functions (37) and (38), respectively.

For a light isotope $\alpha > 1$, the inversion of (36) gives a qualitatively different result:

$$R(t) = A(\alpha) \cos(\omega_0 t) + \varphi(t), \quad \text{if} \quad \alpha > 1.$$  \hfill (40)

Here the function $\varphi(t)$ is still given by equation (39) and vanishes at long times. The resolvent, however, does not vanish and is given for long times by the first term oscillating
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with the frequency and amplitude

$$\omega^* = \frac{\alpha}{\sqrt{2\alpha - 1}} \omega_0 > \omega_0, \quad A(\alpha) = \frac{2\alpha - 2}{2\alpha - 1} < 1.$$  (41)

As discussed in section 6, see equation (25), for a resolvent $R(t)$ non-vanishing at long times the isotope does not reach thermal equilibrium with the bath. Thus the dynamics of a light isotope embedded in a harmonic chain is non-ergodic [18–22].

The results (39)–(41) are well known [18]; in appendix B we give their derivation, i.e. the inversion of the transform (36), in full detail. Note that the initial value of the function $\varphi(t)$ depends on the mass ratio, namely $\varphi(0) = 1$ for $\alpha \leq 1$, and $\varphi(0) = 1 - A(\alpha)$ for $\alpha > 1$. As a result, both expressions (39) and (40) for the resolvent satisfy the initial condition $R(0) = 1$.

The presence of a localized vibrational mode with frequency $\omega^*$ associated with a light isotope is essential for our further discussion. When excited in an isolated lattice, such a vibration does not dissipate by generating running waves but lasts forever as a localized oscillation of the isotope and its neighbours. The phenomenon is similar to localization of electrons in solids around impurity centers. The general condition of normal mode localization is that its frequency $\omega^*$ is outside the frequency spectrum of the undisturbed lattice [18–21]. For a uniform harmonic chain with a single impurity atom that condition is satisfied when the impurity is a light isotope, $\alpha > 1$, see also [18, 20, 21]. On the other hand, for lattice systems with a more complicated composition the localization condition does not necessarily implies $\alpha > 1$ [23–25]. Localized modes may emerge not only due to defects, but also due to the lattice’s anharmonicity [27].

Technically, the emergence of a localized mode can be understood as follows. Given the transform $\hat{R}(s)$, the resolvent $R(t)$ in the time domain is given by the Bromwich integral in the complex plane, $R(t) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{st} \hat{R}(s) ds$. Following the usual routine, one considers a corresponding auxiliary integral $I(t) = \frac{1}{2\pi i} \int e^{st} \hat{R}(s) ds$ over a properly closed contour $\Gamma$, see the right side of figure 4. The integral $I(t)$ can be evaluated using Cauchy’s residue theorem. For a light isotope, $\alpha > 1$, the function $\hat{R}(s)$ given by (36) has simple poles at $\pm i\omega^*$, with $\omega^*$ given by (41), located on the imaginary axis. Then the integral $I(t)$ has components given by the residues Res$[e^{st}\hat{R}(s), i\omega^*]$ and Res$[e^{st}\hat{R}(s), -i\omega^*]$, which oscillate with frequency $\omega^*$. Together these components form the oscillating term in expression (40) for resolvent $R(t)$. Appendix B provides further details.

It may appear from the above reasoning that localization may occur also for a heavy isotope with $1/2 < \alpha \leq 1$, since in that case expression (41) for $\omega^*$ is real and therefore $\hat{R}(s)$ has the poles $\pm i\omega^*$, on the imaginary axis, as for a light isotope. However, one has to take into account that the function $\hat{R}(s)$ given by (36) has two branches, and only one of them is physically meaningful, satisfying the initial condition $R(0) = 1$. As shown in appendix B, for $\alpha \leq 1$ the physical branch of $\hat{R}(s)$ has no poles, and the inversion gives the result (39). Thus, for a heavy isotope and a uniform lattice, $\alpha \leq 1$, there is no localization.

Now equipped with explicit expressions for the resolvent, we can return to the discussion of the energy exchange between the isotope and the bath.
Non-Clausius heat transfer: the example of harmonic chain with an impurity

Figure 2. The average kinetic energy change \( \Delta E(t) = E(t) - E(0) \), in units \( E(0) = T_0 / 2 \), as a function of time for a tagged atom in a uniform lattice, \( \alpha = 1 \), according to equation (42), for different initial temperatures of the atom \( (T_0) \) and the lattice \( (T) \).

7. Uniform lattice and lattice with a heavy isotope

Consider first the case \( \alpha = 1 \) when the system is just a tagged atom in a uniform lattice. The resolvent is given by (37), \( R(t) = J_0(\omega_0 t) \), and expression (33) for the relative energy change function \( \Delta(t) \) takes the form

\[
\Delta E(t) = \frac{1}{2} [1 - J_0^2(\omega_0 t)](T - T_0) + J_1^2(\omega_0 t)T_0
\] (42)

As was noted above, the long time limit, as well as the time average \( \overline{\Delta E} \), of this expression,

\[
\lim_{t \to \infty} \Delta E(t) = \overline{\Delta E} = \frac{1}{2} (T - T_0),
\] (43)

corresponds to Clausius heat transfer for any values of both temperatures. Moreover, while the function \( \Delta E(t) \) is not monotonic, for \( T > T_0 \) (the bath is initially hotter than the isotope), it is positive for any time \( t > 0 \), see figure 2(a).

For \( T = T_0 \), the energy change function (42) is non-negative for any \( t \), see figure 2(b), which corresponds to a non-Clausius heat flow from the bath to the system, despite no
temperatures difference is imposed. At long times, however, $\Delta E(t)$ goes to zero, and so does the heat flow.

For $T < T_0$ (the bath is initially colder than the system), the function $\Delta E(t)$ is positive on the initial and possibly (if the temperature difference is sufficiently small) on later finite time intervals, see figure 2(c). During those intervals the heat transfer is non-Clausius: $\Delta E(t) > 0$ for $T < T_0$ means that the initially hotter system obtains energy from the colder bath. However, at long times $\Delta E(t)$ becomes negative, so that the heat flow turns the direction and becomes Clausius.

For a lattice with a heavy isotope $\alpha < 1$ the situation is qualitatively similar to that for a uniform lattice, $\alpha = 1$. For a hotter lattice $T > T_0$ the heat transfer is Clausius at all times. For a hotter isotope, $T < T_0$, or equal temperatures $T = T_0$, the heat transfer is initially non-Clausius, but becomes Clausius on a longer time scale. Figure 3 illustrates this behavior for a heavy isotope with $\alpha = 1/2$. In that case the resolvent is available in closed form, $R(t) = 2J_1(\omega_0 t)/\omega_0 t$, and the energy change (33) takes the form

$$\Delta E(t) = \frac{1}{2} \left( 1 - \frac{4J_1^2(\omega_0 t)}{\omega_0 t} \right) (T - T_0) + \frac{8}{\omega_0 t} J_2^2(\omega_0 t) T_0. \quad (44)$$

Comparing figures 2 and 3, one observes that the plots for a uniform lattice and a heavy isotope are qualitatively similar, but in the latter case the oscillatory tail of $\Delta E(t)$ decays faster.

For a heavy isotope with other values of the mass ratio $\alpha < 1$ the resolvent $R(t)$ and energy change $\Delta E(t)$ can be evaluated numerically using for the former equation (39). In all cases we observed the same behavior as for $\alpha = 1$ and $\alpha = 1/2$: the heat transfer may be non-Clausius on a short time scale but is back to normal at longer times.

8. Lattice with a light isotope

As discussed in section 6, when the system is a light isotope, $\alpha > 1$, the resolvent has a non-decaying oscillatory component due to the formation of a localized mode, $R(t) = A \cos(\omega_* t) + \varphi(t)$. At long times the function $\varphi(t)$ vanishes, and $R(t) \approx A \cos(\omega_* t)$. Respectively, at long times the energy change function (33) takes the form

$$\Delta E(t) = \frac{1}{2} \left[ 1 - A^2 \cos^2(\omega_* t) \right] (T - T_0) + \frac{1}{\alpha} \left( \frac{\omega_*}{\omega_0} \right)^2 A^2 \sin^2(\omega_0 t) T_0 \quad (45)$$

Taking the time average of this expression, $\overline{\Delta E} = \lim_{t \to \infty} \frac{1}{t} \int_0^t \Delta E(\tau) d\tau$, we obtain the following result

$$\overline{\Delta E} = \frac{1}{2} \left( 1 - \frac{A^2}{2} \right) (T - T_0) + \frac{A^2}{2\alpha} \left( \frac{\omega_*}{\omega_0} \right)^2 T_0 \quad (46)$$

For $T > T_0$ the average energy change of the system is positive, $\overline{\Delta E} > 0$, which corresponds to Clausius heat transfer from the hotter bath to the colder system.

For $T = T_0$ the average energy change of the system is given by the second term of expression (46) and positive, $\overline{\Delta E} > 0$. But now it corresponds to a non-Clausius
heat transfer from the bath to the system, which occurs despite the equality of the temperatures.

The most remarkable situation takes place when the system is hotter than the bath, \( T_0 > T \). In that case it follows from (46) that the direction of the average heat transfer depends on whether the system’s initial temperature \( T_0 \) is higher or lower than the characteristic temperature

\[
T_1 = g_1(\alpha)T > T,
\]

where

\[
g_1(\alpha) = \frac{\alpha(2 - A^2)}{\alpha(2 - A^2) - 2A^2(\omega_*/\omega_0)^2} = \frac{4\alpha^3 - 2\alpha^2 - 2\alpha + 1}{6\alpha^2 - 6\alpha + 1} > 1.
\]

Here in the second equality we used expressions (41) for the frequency \( \omega_* \) and amplitude \( A \) as functions of the mass ratio \( \alpha \). Except when \( \alpha \) is close to one, the factor \( g(\alpha) \) increases approximately linearly. For \( T_0 > T_1 > T \), equation (46) gives \( \Delta E < 0 \) which corresponds to a Clausius heat transfer: the hotter system releases heat to the colder bath. On the other hand, if the initial temperature of the isotope \( T_0 \) is in the interval

\[
T < T_0 < T_1
\]

**Figure 3.** Same as figure 2, but for a heavy isotope with \( \alpha = 1/2 \), according to equation (44).

https://doi.org/10.1088/1742-5468/ab837c
then the time-averaged heat transfer is non-Clausius. In that case one finds from (46)
that $\Delta E > 0$, which suggests that the initially hotter system gets heat from the colder
bath.

9. Conclusion

In this somewhat didactic paper, using the simple model of a harmonic chain of atoms
with a single isotope and imposing a specific initial condition (of the sudden preparation
type), we demonstrate the possibility of non-Clausius heat flow directed from the colder
chain to the hotter isotope. The heat flow also occurs when the initial temperature of
the isotope $T_0$ and that of the chain $T$ are the same.

In the chain with a heavy isotope, and in the uniform lattice, non-Clausius heat
transfer occurs on a relatively short initial time interval or several intervals. At longer
times, the net heat transfer becomes normal, or Clausius: it vanishes when $T = T_0$, and
is directed from a hot subsystem to a cold one when $T \neq T_0$. When averaged over an
asymptotically long time interval, the heat transfer is Clausius.

In contrast, and quite remarkably, in the chain with a light isotope a non-Clausius
heat transfer may occur for all times and does not vanish after averaging over time.

For the presented model, the heat transfer properties correlate with the ergodic ones.
The dynamics of a tagged atom or a heavy isotope embedded in a one-dimensional lattice
is ergodic. For that case, we found that the initial non-Clausius heat flow vanishes on
long time scales. On the other hand, the dynamics of a light isotope in a harmonic chain
is not ergodic. For that case, non-Clausius heat transfer does not vanish at longer times.

Our findings appear to corroborate the general arguments of references [1–5]: the
temperatures of two initially isolated systems $A$ and $B$ do not completely define the
dynamics of the energy flow in the composite system $AB$. As a result, the heat transfer
between $A$ and $B$ may be non-Clausius on short or even, in special cases, long time
scales.

On the other hand, it remains to be seen to what extent our findings are generic
or due to specific features of the exploited model. Besides being integrable, the model
has other peculiarities which make it somewhat ambiguous to interpret the results in
terms of thermodynamic quantities. In particular, in this paper we defined the direction
of heat transfer based on the sign of the change of the system’s kinetic energy $E(t)$.
In general, one would prefer to use the system’s internal energy $U(t)$ instead of $E(t)$. It
is natural to identify the former as the average of the part of the total Hamiltonian
which depends on dynamical variables of the system only. In our model, that part is $H_s =
P^2/(2M) + kQ^2$, so that $U(t) = \langle H_s \rangle = E(t) + k\langle Q^2(t) \rangle$. At $t = 0$, such a definition of the
internal energy takes the reasonable value $U(0) = T_0$. However, for an infinite lattice the
component $k\langle Q^2(t) \rangle$ can be shown to diverge in the limit $t \to \infty$ and thus cannot model
a physically meaningful contribution to the system’s internal energy. The divergence of
the of mean-square displacement $\langle Q^2(t) \rangle$ is by no means an unphysical result, but reflects
the delocalization of a particle embedded in an infinite one-dimensional harmonic lattice
[10, 14, 18, 24]. The divergence of $U(t)$ could be removed by including the energy of
interaction with the bath, but in that case $U(t)$ would depend on bath variables as well
and could hardly be qualified as an internal energy of the system. One may hope to

https://doi.org/10.1088/1742-5468/ab837c
resolve these difficulties and limitations with models more elaborate than the simple one presented here.

Appendix A

In this appendix we derive the generalized Langevin equation (10) for the isotope for the setting depicted in figure 1 and described in section 2. The first step is to diagonalize the Hamiltonian \( H_b = H_r + H_l \) of the bath, equation (4). Consider the Hamiltonian \( H_r \) of the right part of the bath, equation (5),

\[
H_r = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{k}{2} \left\{ q_i^2 + (q_2 - q_1)^2 + \cdots + (q_N - q_{N-1})^2 + q_N^2 \right\}. \tag{A1}
\]

It can be recognized as the Hamiltonian of the chain of \( N+1 \) atoms with fictitious terminal atoms \( i = 0 \) and \( i = N+1 \), whose momenta and displacements are fixed to be zero, \( p_0 = p_{N+1} = q_0 = q_{N+1} = 0 \),

\[
H_r = \frac{1}{2m} \sum_{i=1}^{N} p_i^2 + \frac{k}{2} \sum_{i=0}^{N} (q_{i+1} - q_i)^2. \tag{A2}
\]

For this Hamiltonian the normal mode transformation \( \{ q_i, p_i \} \leftrightarrow \{ Q_j, P_j \} \) is well-known to have the form

\[
q_i = \frac{1}{\sqrt{m}} \sum_{j=1}^{N} A_{ij} Q_j, \quad p_i = \sqrt{m} \sum_{j=1}^{N} A_{ij} P_j, \quad i = 1, 2, \ldots N \tag{A3}
\]

with the transition matrix

\[
A_{ij} = \sqrt{\frac{2}{N+1}} \sin \frac{\pi ij}{N+1}, \quad i, j = 1, 2, \ldots N \tag{A4}
\]

satisfying the orthogonality relation \( \sum_{i=1}^{N} A_{ij} A_{i'j'} = \delta_{jj'} \). In terms of new coordinates \( \{ Q_j \} \) and momenta \( \{ P_j \} \) the Hamiltonian \( H_r \) is diagonalized into a sum of \( N \) independent normal modes with frequencies \( \omega_j \),

\[
H_r = \frac{1}{2} \sum_{j=1}^{N} \left\{ P_j^2 + \omega_j^2 Q_j^2 \right\}, \quad \omega_j = \omega_0 \sin \frac{\pi j}{2(N+1)}, \tag{A5}
\]

where \( \omega_0 = 2\sqrt{k/m} \).

A similar expression one finds also for the Hamiltonian \( H_l \) of the left part of the bath,

\[
H_l = \frac{1}{2} \sum_{s=1}^{N} \left\{ P_s^2 + \omega_s^2 Q_s^2 \right\}, \quad \omega_s = \omega_0 \sin \frac{\pi s}{2(N+1)}. \tag{A6}
\]

Here and below we use indices \( 1 \leq j \leq N \) and \( 1 \leq s \leq N \) to refer to normal modes for the right and left parts of the bath, respectively.
The coupling Hamiltonian \( H_c \) given by equation (7),
\[
H_c = -k(q_1 + q_{-1})Q,
\]
in terms of normal modes takes the form
\[
H_c = -\left\{ \sum_{j=1}^{N} c_j Q_j + \sum_{s=1}^{N} c_s Q_s \right\} Q,
\]
with the coupling coefficients for the right bath
\[
c_j = \frac{k}{\sqrt{m}} A_{1j} = \frac{k}{\sqrt{m}} \sqrt{\frac{2}{N+1}} \sin \frac{\pi j}{N+1},
\]
and similar expressions for the coupling coefficients \( c_s \) for the left bath.

The equation of motion for the isotope
\[
\dot{P} = -\frac{\partial H}{\partial Q} = -2kQ + k(q_1 + q_{-1})
\]
in terms of normal coordinates takes the form
\[
\dot{P} = -2kQ + \sum_{j=1}^{N} c_j Q_j + \sum_{s=1}^{N} c_s Q_s.
\]

Our goal is to find explicit expressions for normal modes \( \{ Q_j, Q_s \} \), to substitute them into the above equation of motion of the isotope, and to present the latter in the Langevin form.

The equations of motions for the normal modes of the right part of the bath read
\[
\dot{P}_j = -\frac{\partial H}{\partial Q_j} = -\omega_j^2 Q_j + c_j Q_j, \quad \dot{Q}_j = \frac{\partial H}{\partial P_j} = P_j.
\]

Differentiating the second of these equations and substituting into the first one yields equations for \( Q_j \),
\[
\ddot{Q}_j + \omega_j^2 Q_j = c_j Q_j.
\]

Solving these equations using, for instance, the method of Laplace transform, one finds
\[
Q_j(t) = Q_j^0(t) + \frac{c_j}{\omega_j} \int_0^t \sin(\omega_j \tau)Q(t - \tau) d\tau.
\]
Here \( Q_j^0(t) \) is the general solution of the homogeneous equation \( \ddot{Q}_j + \omega_j^2 Q_j = 0 \),
\[
Q_j^0(t) = Q_j(0) \cos(\omega_j t) + \frac{P_j(0)}{\omega_j} \sin(\omega_j t).
\]
Integrating by parts, expression (A14) can be written in terms of the isotope’s momentum $P = M \dot{Q}$,

$$Q_j(t) = Q_j^0(t) + \frac{c_j}{\omega_j} \left\{ Q(t) - Q(0) \cos(\omega_j t) - \frac{1}{M} \int_0^t \cos(\omega_j \tau) P(t - \tau) d\tau \right\}. \quad (A16)$$

Substitution of this and a similar expression for the left normal modes $Q_s$ in the impurity’s equation of motion (A11), yields the generalized Langevin equation

$$\dot{P}(t) = -\int_0^t K(t - \tau) P(\tau) + \xi(t) - MQ(0)K(t) - k_s Q(t) \quad (A17)$$

where the memory kernel $K(t)$ and stochastic force $\xi(t)$ are given by the expressions

$$K(t) = \frac{1}{M} \sum_{j=1}^N \left( \frac{c_j}{\omega_j} \right)^2 \cos(\omega_j t) + \frac{1}{M} \sum_{s=1}^N \left( \frac{c_s}{\omega_s} \right)^2 \cos(\omega_s t), \quad (A18)$$

$$\xi(t) = \sum_{j=1}^N c_j Q_j^0(t) + \sum_{s=1}^N c_s Q_s^0(t), \quad (A19)$$

with $Q_j^0(t)$ and $Q_s^0(t)$ given by (A15).

Equation (A17) contains the initial slip force $-MQ(0)K(t)$ and the linear force $-k_s Q(t)$ with the $N$-dependent spring constant

$$k_s = 2k - \sum_{j=1}^N \left( \frac{c_j}{\omega_j} \right)^2 - \sum_{s=1}^N \left( \frac{c_s}{\omega_s} \right)^2. \quad (A20)$$

The force $-k_s Q(t)$ tends to localize the isotope about its equilibrium position $Q = 0$. It disappears in the limit of the infinite chain. Indeed, with (A5), (A6) and (A9) one finds

$$\sum_{j=1}^N \left( \frac{c_j}{\omega_j} \right)^2 = \sum_{s=1}^N \left( \frac{c_s}{\omega_s} \right)^2 = \frac{N}{N+1} k. \quad (A21)$$

Then it follows from (A20) and (A21) that $k_s \to 0$ as $N \to \infty$, and the Langevin equation (A17) takes the form (10), exploited in the main text,

$$\dot{P}(t) = -\int_0^t K(t - \tau) P(\tau) + \xi(t) - MQ(0)K(t). \quad (A22)$$

In order to interpret (A17) as a Langevin equation one needs to define statistical properties of the stochastic force $\xi(t)$ with respect to an appropriate ensemble. In this paper we assume that the lattice at $t \leq 0$ is in the state of constrained equilibrium, see figure 1, with the isotope kept fixed in the equilibrium position. Respectively, we define the average of an arbitrary dynamical variable $A$ over the initial coordinates and momenta of the bath

$$\langle A \rangle = \int \prod_j dQ_j dP_j \prod_s dQ_s dP_s (\rho_b A) \quad (A23)$$

https://doi.org/10.1088/1742-5468/ab837c
with the canonical distribution (8),
\[ \rho_b = Z^{-1}e^{-H_b/T} = (Z_r^{-1}e^{-H_r/T})(Z_l^{-1}e^{-H_l/T}). \] (A24)

Then it is straightforward to show that \( \xi(t) \) can be interpreted as a stochastic process which is zero-centered, stationary, and satisfying the standard fluctuation-dissipation relation,
\[ \langle \xi(t) \rangle = 0, \langle \xi(t)\xi(t') \rangle = \langle \xi(0)\xi(t-t') \rangle, \langle \xi(t)\xi(t') \rangle = MTK(t-t'). \] (A25)

As a final step, let us derive an expression for the kernel \( K(t) \), equation (A18), in the limit of the infinite lattice. Taking into account the expressions for \( c_j \) and \( \omega_j \) one finds
\[ \left( \frac{c_j}{\omega_j} \right)^2 = \frac{2k}{N+1} \cos^2 \left( \frac{\pi}{2} \frac{j}{N+1} \right) = \frac{2k}{N+1} \cos^2(\varphi_j), \] (A26)
where we introduced the discrete variable
\[ \varphi_j = \frac{\pi}{2} \frac{j}{N+1}. \] (A27)

Substitution of (A26) into (A18) yields
\[ K(t) = \frac{k}{\sinh^2 \frac{\pi}{2} (N+1)} \sum_{j=1}^{N} \cos^2(\varphi_j) \cos(\omega_0 t \sin(\varphi_j)). \] (A28)

With \( \Delta \varphi = \varphi_n - \varphi_{n-1} = \frac{\pi}{2N+1} \), the above expression can be written as
\[ K(t) = \frac{k}{\sinh^2 \frac{\pi}{2} (N+1)} \sum_{j=1}^{N} \cos^2(\varphi_j) \cos(\omega_0 t \sin(\varphi_j)) \Delta \varphi. \] (A29)

In the limit of the infinite chain, \( N \to \infty \), the above expression takes the integral form
\[ K(t) = \frac{\alpha \omega_0^2}{2} \frac{2}{\pi} \int_0^{\pi/2} \cos^2(\varphi) \cos(\omega_0 t \sin \varphi) d\varphi, \] (A30)
where \( \alpha = m/M \). The evaluation of the integral gives the expression for the kernel in terms of Bessel functions
\[ K(t) = \frac{\alpha \omega_0}{t} J_1(\omega_0 t) = \frac{\alpha \omega_0^2}{2} \left\{ J_0(\omega_0 t) + J_2(\omega_0 t) \right\}. \] (A31)

This is expression (12) of the main text.

Appendix B

In this appendix we perform the inversion of the resolvent’s Laplace transform (36),
\[ \tilde{R}(s) = \frac{1}{\alpha \sqrt{s^2 + \omega_0^2} + (1 - \alpha)s} \] (B1)

https://doi.org/10.1088/1742-5468/ab837c
for arbitrary values of the mass ratio $\alpha = m/M$. As discussed in section 4, expression (B1) also gives the Laplace transform for the equilibrium correlation function $C(t)$ given by (18), which was the subject of many studies. Although the result is well known [18], the inversion is not without subtlety and perhaps deserves to be discussed in a didactic manner.

The inversion of (B1) is given by the Bromwich integral

$$R(t) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{st} \tilde{R}(s) \, ds.$$  

(B2)

The function $\tilde{R}(s)$ has two branches, which we shall denote as $\tilde{R}_1(s)$ and $\tilde{R}_2(s)$ and write as

$$\tilde{R}_k(s) = \frac{1}{\alpha f_k(s) + (1 - \alpha)s}, \quad k = 1, 2$$  

(B3)

where $f_1(s)$ and $f_2(s)$ are the two branches of the square-root function

$$f(s) = \sqrt{s^2 + \omega_0^2} = \sqrt{s + i\omega_0} \sqrt{s - i\omega_0}.$$  

(B4)

It is convenient to write in the last expression $s \pm i\omega_0$ in a polar form

$$s - i\omega_0 = r_1 e^{i\theta_1}, \quad s + i\omega_0 = r_2 e^{i\theta_2},$$  

(B5)

with polar coordinates $(r_k, \theta_k)$ defined on the left side of figure 4. Then we can define the two branches of $f(s)$ by the expression

$$f_k(s) = r_1 r_2 e^{i(2\pi k/2)} e^{i\theta_k}, \quad k = 1, 2$$  

(B6)

where the ranges of arguments $\theta_1$ and $\theta_2$ for the first branch $f_1(s)$ are the same

$$-\frac{3\pi}{2} < \theta_1 < \frac{\pi}{2}, \quad -\frac{3\pi}{2} < \theta_2 < \frac{\pi}{2}.$$  

(B7)

while for the second branch $f_2(s)$

$$-\frac{3\pi}{2} < \theta_1 < \frac{\pi}{2}, \quad \frac{\pi}{2} < \theta_2 < \frac{5\pi}{2}.$$  

(B8)

As easy to verify, the two functions $f_1(s)$ and $f_2(s)$ defined in this way are continuous at any $s$ except on the branch cut along the imaginary axis connecting the two branch points $\pm i\omega_0$. On the branch cut both branches $f_1(s)$ and $f_2(s)$ are discontinuous. It is instructive to identify the following mapping rules for the functions $f_1(s)$ and $f_2(s)$:

(a) Let $s = x > 0$ be real and positive. Then $f_1(s)$ is also real and positive, while $f_2(s)$ is real and negative.

(b) Let $s = -x < 0$ be real and negative. Then $f_1(s)$ is also real and negative, while $f_2(s)$ is real and positive.

(c) Let $s = iy, \ y > 0$ be on the positive part of the imaginary axis. Then $f_1(s)$ and $f_2(s)$ are on the positive and negative parts of the imaginary axis, respectively.
(d) Let $s = -iy$, $y > 0$ be on the negative part of the imaginary axis. Then $f_1(s)$ and $f_2(s)$ are on the negative and positive parts of the imaginary axis, respectively.

Let us show that only one branch of the function $\tilde{R}(s)$ is physically meaningful. Indeed, according to (17), $R(0) = 1$. Then, using the initial value theorem, we get the condition

$$R(0) = \lim_{s \to \infty} s \tilde{R}(s) = \lim_{s \to \infty} \frac{s}{\alpha \sqrt{s^2 + \omega_0^2} + (1 - \alpha)s} = 1. \quad (B9)$$

As follows from the mapping rules above, condition (B9) is only satisfied if the two-value function $f(s) = \sqrt{s^2 + \omega_0^2}$ in the denominator is represented by the first branch $f_1(s)$. Therefore the Bromwich integral (B2) should be evaluated with the first branch of the function $\tilde{R}(s)$,

$$R(t) = \frac{1}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} e^{st} \tilde{R}_1(s) ds, \quad \tilde{R}_1(s) = \frac{1}{\alpha f_1(s) + (1 - \alpha)s}. \quad (B10)$$

Below we shall refer to the branches $\tilde{R}_1(s)$ and $\tilde{R}_2(s)$ as physical and unphysical, respectively.
For $\alpha \neq 1$, the function $\tilde{R}(s)$ given by (B1) has two poles at positions $s_1$ and $s_2$ which satisfy the equation

$$\alpha \sqrt{s^2 + \omega_0^2} + (1 - \alpha)s = 0. \quad (B11)$$

The solutions

$$s_{1,2} = \pm i \frac{\alpha}{\sqrt{2\alpha - 1}} \omega_0 \quad (B12)$$

are purely imaginary for $\alpha > 1/2$, and real for $\alpha < 1/2$.

One can show that expression (B12) defines the poles for the physical branch $\tilde{R}_1(s)$ only for $\alpha > 1$, i.e. for a light isotope, while for $\alpha \leq 1$ expression (B12) gives the poles for the unphysical branch $\tilde{R}_2(s)$. Indeed, let us rewrite equation (B11) as

$$f(s) = \sqrt{s^2 + \omega_0^2} = -\frac{1 - \alpha}{\alpha}s. \quad (B13)$$

Consider first the case $\alpha > 1/2$ when equation (B12) predicts the poles located on the imaginary axis. Consider the pole at $s_1 = iy$, $y > 0$, which is on the positive part of the imaginary axis. As follows from (B13), $f(s_1) = \sqrt{s_1^2 + \omega_0^2}$ must have a value on the negative and positive parts of the imaginary axis for $\alpha < 1$ and $\alpha > 1$, respectively. According to mapping rule (c), $f(s)$ must be represented by the branch $f_2(s)$ for $\alpha < 1$ and by the branch $f_1(s)$ for $\alpha > 1$. Therefore, the pole at $s_1 = iy$, $y > 0$ is the one for the unphysical branch $\tilde{R}_2(s)$ if $1/2 < \alpha < 1$ and for the physical branch $\tilde{R}_1(s)$ if $\alpha > 1$.

The same conclusion we arrive at, now taking into account mapping rule (d), for a pole at $s_2 = -iy$, $y > 0$ located on the negative imaginary axis.

Consider now the case $\alpha < 1/2$, when equation (B12) predicts the poles located on the real axis. Consider the pole at $s_1 = x > 0$ located on the positive part of the real axis. As one observes from (B13), in that case $f(s_1) = \sqrt{s_1^2 + \omega_0^2}$ must have a value on the negative part of the real axis. According to mapping rule (a), this is only possible if $f(s)$ is represented by the branch $f_2(s)$. Therefore, for $\alpha < 1/2$ the pole located on the positive part of the real axis is a pole for the unphysical branch $\tilde{R}_2(s)$. Similarly, using mapping rule (b), one verifies that the second pole at $s_2 = -x < 0$ is also a pole for the unphysical branch $\tilde{R}_2(s)$.

Summarizing, for a light isotope, $\alpha > 1$, the physical branch $\tilde{R}_1(s)$ of the resolvent’s transform has two branch points $\pm i\omega_0$ and two poles on the imaginary axis

$$s_{1,2} = \pm i\omega_*, \quad \omega_* = \frac{\alpha}{\sqrt{2\alpha - 1}} \omega_0 > \omega_0. \quad (B14)$$

For a heavy isotope, $\alpha < 1$, and a uniform lattice $\alpha = 1$, the function $\tilde{R}_1(s)$ has two branch points $\pm i\omega_0$ and no poles. Since all singular points of $\tilde{R}_1(s)$ are on the imaginary axis, the integration in (B10) is along an arbitrary vertical line to the right of the origin.

The remaining steps are standard. In order to evaluate the Bromwich integral (B10), consider an auxiliary integral

$$I(t) = \frac{1}{2\pi i} \int_\Gamma e^{st} \tilde{R}_1(s)\,ds \quad (B15)$$

https://doi.org/10.1088/1742-5468/ab837c
over the closed contour $\Gamma$ shown on the right in figure 4. The contributions to $I$ from the large semi-arc of radius $R$ and small circles of radius $\epsilon$ about branch points $\pm i\omega_0$ vanish when $R \to \infty$ and $\epsilon \to 0$. The contribution from the two horizontal lines above and below the real axis vanishes as well as the distance between the lines goes to zero. The only two non-zero contributions to $I = I_1 + I_2$ come from the integration over:

(a) The two sides of the vertical branch cut connecting the branch points $\pm i\omega_0$ ($I_1$),
(b) The rightmost vertical segment ($I_2$).

In the limit $R \to \infty$, the contribution $I_2$ equals $R(t)$, so one gets $I = I_1 + R(t)$. On the other hand, according to Cauchy’s theorem, the integral $I$ equals to the sum of residues at the poles inside $\Gamma$,

$$I(t) = I_1(t) + R(t) = h(\alpha - 1) \left\{ \text{Res}[e^{st}\tilde{R}_1(s), i\omega_*] + \text{Res}[e^{st}\tilde{R}_1(s), i\omega_*] \right\}. \quad (B16)$$

Here the step function $h(x)$ is defined as

$$h(x) = \begin{cases} 1, & \text{if } x > 0 \\ 0, & \text{if } x \leq 0. \end{cases} \quad (B17)$$

The appearance of $h(\alpha - 1)$ in (B16) reflects that $\tilde{R}_1(s)$ has the poles inside $\Gamma$ only for a light isotope $\alpha > 1$. As discussed above, for $\alpha \leq 1$ the function $\tilde{R}_1(s)$ has no singularities inside $\Gamma$, so that $I = 0$. From (B16) one gets,

$$R(t) = h(\alpha - 1) \left\{ \text{Res}[e^{st}\tilde{R}_1(s), i\omega_*] + \text{Res}[e^{st}\tilde{R}_1(s), i\omega_*] \right\} - I_1(t). \quad (B18)$$

Consider first the integral $I_1(t)$, which has two contributions, $I_1 = I_1^- + I_1^+$. The contribution $I_1^-$ is the integral over the vertical path just left from the branch cut, i.e. from $-i\omega_0 - \epsilon$ to $i\omega_0 - \epsilon$ with infinitesimal $\epsilon > 0$. Using the path parameterization $s = iy - \epsilon$ with $-\omega_0 < y < \omega_0$, one gets

$$I_1^- = \frac{1}{2\pi} \int_{-\omega_0}^{\omega_0} e^{st} \tilde{R}_1(s) s' (y) dy = \frac{1}{2\pi} \int_{-\omega_0}^{\omega_0} e^{st} \frac{e^{iy\sqrt{\omega_0^2 - y^2}}}{\alpha f_1(s) + (1 - \alpha)s} dy. \quad (B19)$$

According to (B6) and (B7), on the given path

$$f_1(s) = -\sqrt{\tau_1 r_2} = -\sqrt{(\omega_0 - y)(\omega_0 + y)} = -\sqrt{\omega_0^2 - y^2}. \quad (B20)$$

Then

$$I_1^- = \frac{1}{2\pi} \int_{-\omega_0}^{\omega_0} \frac{e^{iy\sqrt{\omega_0^2 - y^2}}}{\alpha \sqrt{\omega_0^2 - y^2} + i(1 - \alpha)y} dy. \quad (B21)$$

Similarly, one can evaluate the contribution $I_1^+$ which is the integral over the right side of the branch cut, from $i\omega_0 + \epsilon$ to $-i\omega_0 + \epsilon$. Now the path is parameterized as $s = iy + \epsilon$, and $f_1(s) = \sqrt{\tau_1 r_2} = \sqrt{\omega_0^2 - y^2}$, which gives

$$I_1^+ = \frac{1}{2\pi} \int_{\omega_0}^{\omega_0} e^{iy\sqrt{\omega_0^2 - y^2}} dy = \frac{1}{2\pi} \int_{-\omega_0}^{\omega_0} e^{iy\sqrt{\omega_0^2 - y^2}} dy. \quad (B22)$$
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Adding (B21) and (B22), and taking into account that the contribution from the odd part of the integrand is zero, yields

$$I_1(t) = -\frac{2\alpha}{\pi} \int_0^{\omega_0} \frac{\sqrt{\omega_0^2 - y^2} \cos(yt)}{(1 - 2\alpha)y^2 + \alpha^2 \omega_0^2} dy.$$  \hspace{1cm} (B23)

It remains to evaluate the residues in equation (B18). One can verify that the pole at $s_1 = i\omega_*$ is the pole of first order, so that

$$\text{Res}[e^{st}\tilde{R}_1(s), i\omega_*] = \lim_{s \to i\omega_*} e^{st}\tilde{R}_1(s) - i\omega_* = \lim_{s \to i\omega_*} \frac{e^{st}(s - i\omega_*)}{\alpha f_1(s) + (1 - \alpha)s}. \hspace{1cm} (B24)$$

Evaluating the limit with L’Hospital’s rule one gets

$$\text{Res}[e^{st}\tilde{R}_1(s), i\omega_*] = \frac{\alpha - 1}{2\alpha - 1} e^{i\omega_* t}. \hspace{1cm} (B25)$$

Similarly, for the residue at the second pole one obtains

$$\text{Res}[e^{st}\tilde{R}_1(s), -i\omega_*] = \frac{\alpha - 1}{2\alpha - 1} e^{-i\omega_* t}. \hspace{1cm} (B26)$$

Finally, the substitution of (B23), (B25) and (B26) into (B18) yields for the resolvent the following expression

$$R(t) = h(\alpha - 1)A(\alpha) \cos(\omega_* t) + \varphi(t), \hspace{1cm} (B27)$$

were the amplitude of the oscillatory term equals

$$A(\alpha) = \frac{2\alpha - 2}{2\alpha - 1}, \hspace{1cm} (B28)$$

the function $\varphi(t) = -I_1(t)$ is given by the integral

$$\varphi(t) = \frac{2\alpha}{\pi} \int_0^{\omega_0} \frac{\sqrt{\omega_0^2 - y^2} \cos(yt)}{(1 - 2\alpha)y^2 + \alpha^2 \omega_0^2} dy,$$  \hspace{1cm} (B29)

and the step function $h(x)$ is defined by equation (B17). The result (B27) is equivalent to equations (39) and (40) of the main text.

As discussed in section 6, the function $\varphi(t)$ can be expressed in closed form in terms of Bessel functions for $\alpha = 1$ and $\alpha = 1/2$. One can verify that $\varphi(t) \to 0$ as $t \to \infty$ for any value of the mass ratio $\alpha$.

For the purpose of the present paper, the most remarkable feature of expression (B27) is that for a light isotope ($\alpha > 1$) the resolvent $R(t)$ does not vanish at long times but oscillates with the (localized mode) frequency $\omega_* = \alpha \omega_0 / \sqrt{2\alpha - 1}$. For a heavy isotope or a uniform lattice ($\alpha \leq 1$) localization does not occur, and the resolvent $R(t)$ is given by the decaying function $\varphi(t)$. 

https://doi.org/10.1088/1742-5468/ab837c
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