A heat pump at a molecular scale controlled by a mechanical force

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Abstract. – We show that a mesoscopic system such as Feynman’s ratchet may operate as a heat pump, and clarify underlying physical picture. We consider a system of a particle moving along an asymmetric periodic structure. When put into contact with two distinct heat baths of equal temperature, the system transfers heat between two baths as the particle is dragged. We examine Onsager relation for the heat flow and the particle flow, and show that the reciprocity coefficient is a product of the characteristic heat and the diffusion constant of the particle. The characteristic heat is the heat transfer between the baths associated with a barrier-overcoming process. Because of the correlation between the heat flow and the particle flow, the system can work as a heat pump when the particle is dragged. This pump is particularly effective at molecular scales where the energy barrier is of the order of the thermal energy.

Introduction. – In the last decade, physics and technology have moved more and more toward the manipulation of mesoscopic objects. Techniques of micro manipulation of molecules are expanding to open new possibilities to future technology. Although to control heat flow in mesoscopic scales may be among crucial issues, its study is still in a preliminary stage [1]. Heat pumps working in nano-scale devices [2, 3] or mesoscopic machines [4] are studied but the number of cases are still limited. In this letter, we study a class of mesoscopic systems working as a heat pump and present a physical picture explaining how they work. We start from a numerical study adopting one specific model, and demonstrate that a characteristic heat in a barrier-overcoming process determines the ability of the heat pump and Onsager’s reciprocity coefficients. Then, we give a theoretical derivation of the reciprocity coefficients and show the generality of the results in a class of Feynman’s ratchet [5]. We present a simple and clear picture for the mechanism of heat pumps, which is expected to be useful in designing various mesoscopic heat pumps.

Model. – We study a class of systems including Feynman’s ratchet in which a particle moves along a periodic structure. The particle interacts with the periodic structure in an asymmetric manner. The periodic structure and the particle are attached to distinct heat baths \(B_1\) and \(B_2\), whose temperatures are \(T_1\) and \(T_2\), respectively. We start from a specific
but typical model shown in fig. 1 [6], which is suitable for numerical simulation. In this model, a one-dimensional harmonic lattice corresponds to the periodic structure. The time evolution of the system is described by a set of Langevin equations,

\[ \ddot{x}_i = -\gamma \dot{x}_i + \sqrt{2\gamma T_1} \xi_i(t) - \frac{\partial (V_{\text{as}} + V_i)}{\partial x_i}, \quad \ddot{x}_p = -\gamma \dot{x}_p + \sqrt{2\gamma T_2} \xi_p(t) - \frac{\partial V_{\text{as}}}{\partial x_p} + f, \]

where \( x_p \) and \( x_i \) are the positions of the particle and the \( i \)-th lattice site (\( i = 1, \cdots, N_c \)). An external force \( f \) is applied to the particle. \( \gamma \) is the friction constant and \( \xi_\alpha(t) \) is the random force satisfying \( \langle \xi_\alpha(t) \rangle = 0 \) and \( \langle \xi_\alpha(t) \xi_\beta(t') \rangle = \delta_{\alpha,\beta} \delta(t-t') \). The interaction between the particle and the lattice sites is described by the asymmetric potential \( V_{\text{as}} = \sum_i v_{\text{as}}(x_p - x_i) \) with \( v_{\text{as}} \) as in fig. 1. \( V_i = \sum_i v_o(x_i - x_{i0}) + v_c(x_{i+1} - x_i) \) is the harmonic potential for the lattice, where \( v_o(x) = K_c x^2/2 \) is the on-site potential and \( v_c(x) = K_c(x - l)^2/4 \) is the interaction between neighbors. \( l \) is the lattice interval, \( x_{i0} = il \) for \( i \)-th site, and \( K_c \) is a parameter for stiffness. When \( K_c \) is sufficiently large, the lattice does not fluctuate and the potential for the particle reduces to a one-dimensional sawtooth-shaped potential.

On this periodic structure, the particle performs stepwise motions with a typical step size \( l \). At sufficiently low temperatures, each stepwise motion occurs stochastically with a dwell time long enough for the particle to lose its memory. In equilibrium, the probabilities of rightward and leftward steps are of course identical. In the following, we concentrate on nonequilibrium steady states maintained by an external force and/or a temperature difference.

**Heat flow induced by particle motion and Onsager relation.** Temporal heat flows from the heat baths to the system are defined for each trajectory by using the stochastic energetics [7, 8] as

\[ \dot{J}_1(t) = \sum_i [-\gamma \dot{x}_i + \sqrt{2\gamma T_1} \xi_i(t)] \circ \dot{x}_i, \quad \dot{J}_2(t) = [-\gamma \dot{x}_p + \sqrt{2\gamma T_2} \xi_p(t)] \circ \dot{x}_p, \]

where \( \dot{J}_1(t) \) is the heat flow from \( B_1 \) to the system and \( \dot{J}_2(t) \) is that from \( B_2 \) to the system. From eq. (2), we define temporal heat flow between the two heat baths as

\[ \dot{J}_q(t) \equiv (\dot{J}_2(t) - \dot{J}_1(t))/2. \]

In the steady states, mean heat flows \( J_1 \equiv \langle \dot{J}_1(t) \rangle, J_2 \equiv \langle \dot{J}_2(t) \rangle \) and \( J_q \equiv \langle \dot{J}_q(t) \rangle \) can be defined, where \( \langle \cdot \rangle \) denotes average over time and ensemble.
When a steady external force $f$ is applied to the particle, energy corresponding to the mechanical work by $f$ is provided to the system. Its mean rate is

$$\dot{W} \equiv \langle \dot{x}_p f \rangle = J_p f,$$

where $J_p$ is the mean particle flow defined as $J_p \equiv \langle \dot{x}_p \rangle$. In the steady states, the energy of the system remains constant on average. This constraint leads to the balance of the energy flows $\dot{W}$, $J_1$ and $J_2$ as in fig. 1(b), and implies $\dot{W} = -(J_1 + J_2)$.

Let $T_1 = T_2$. When the particle is dragged, the particle and the sites are expected to warm up due to the friction. Then one expects that heat transfer from the hot components to their surroundings takes place, and that $J_1 < 0$ and $J_2 < 0$. Contrary to this expectation, $J_1$ or $J_2$ can be positive for small values of $f$ in fig. 2(a). The system then works as a heat pump which absorbs energy from one of the heat baths and dissipates it to the other.

Figure 2(b) shows that the heat flow $J_q$ depends linearly on $f$ in a wide range, including the region with $J_1, J_2 > 0$ (see fig. 2(a)). The particle flow $J_p$ also shows a linear dependence on $f$ in a comparable range. Since the range in which the system works as a heat pump is included in this linear range, we are led to study Onsager relation [9] for $J_p$ and $J_q$. Define $T$ and $\Delta T$ by $T_1 = T - \Delta T/2$ and $T_2 = T + \Delta T/2$. Thermodynamic forces for the flows $J_p$ and $J_q$ are $f/T$ and $\Delta T/T^2$, respectively. Onsager relations are formally written as,

$$J_p = L_{pp} \frac{f}{T} + L_{pq} \frac{\Delta T}{T^2}, \quad J_q = L_{qp} \frac{f}{T} + L_{qq} \frac{\Delta T}{T^2}.$$  (5)

The coefficients are written as

$$L_{pp} = D_p, \quad L_{qq} = T^2 \lambda, \quad L_{qp} = L_{pq} = q^{eq} D_p / l,$$  (6)

where $D_p$ is the diffusion constant for the particle in equilibrium, $\lambda \equiv \partial J_q / \partial \Delta T$ is the heat conductivity of the system and $q^{eq}$ is the characteristic heat which will be discussed in the next section. To derive the expression for $L_{pp}$, we define the mobility as $\mu \equiv \partial J_p / \partial f$. Then Einstein’s relation $\mu = D_p / T$ implies $L_{pp} = \mu T = D_p$. The expression for $L_{qq}$ follows from the definition. The expressions for the off-diagonal coefficients $L_{qp}$ and $L_{pq}$ will be derived in the following (see (7) and (10)).

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(1) If the system is not in overdamped limit, the mechanical force can make some part of the system cool down. When $J_2 > 0$, kinetic temperature of the particle is lower than $T_2$ and, when $J_1 > 0$, that for the lattice sites lower than $T_1$. 

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Characteristic heat associated with barrier-overcoming process. – In this section, we investigate a characteristic heat associated with a barrier-overcoming process in the vicinity of the equilibrium states. It enables us to determine the non-diagonal coefficients $L_{qp}$ and $L_{pq}$. First, let us consider equilibrium cases. When the system exhibits a stepwise motion, it should overcome an energy barrier. To reach the top of the barrier the system absorbs some amount of heat from the two heat baths and dissipates the same amount of heat to descend from the top (fig. 3). In equilibrium, of course, no net heat transfer occurs between the baths on average. But if we take the ensemble averages of the heat transfer for the individual steps classifying the rightward and the leftward steps, nonvanishing heat transfer between the two baths can survive. We find that a single rightward step carries heat $q_R$ and a leftward step carries $q_L$ on average. In equilibrium, the rightward and the leftward stepwise motions occur with the equal probability and the relation $q_R = -q_L \equiv q^{eq}$ holds, which consistently leads to vanishing of net heat transfer between the two heat baths. In general, nonvanishing values of $q^{eq}$ are obtained [10], because it comes from left-right asymmetry of the system.

Next, consider the case where a small external force $f$ is applied under the isothermal condition $\Delta T = 0$. From the measurement of $J_p$ and $J_q$, we can define a characteristic heat $q_c \equiv J_q/(J_p/l)$ in the linear region of $J_p$ and $J_q$. Because $J_p/l$ is the net number of directed steps per unit time, $q_c$ is conjectured to be a heat transferred per single directed step. By determining the value of $q_c$ and $q^{eq}$ separately from numerical simulation, we have observed $q_c \approx q^{eq}$ for sufficiently small $f$ (see fig. 4(a)). This implies that the characteristic heat $q_c$ associated with the stepwise motion in the linear region is the characteristic heat $q^{eq}$ at the equilibrium states. Then, we obtain

$$J_q = \frac{\mu q^{eq} f}{l} = \frac{q^{eq} D_p f}{l T},$$

(7)

by substituting $J_p = \mu f$ into $J_q/(J_p/l) = q^{eq}$. Equation (7) holds for a wide range of the model parameter $K_c$ as is examined in fig. 4(b), where $\chi_q \equiv J_q/f$. Thus the non-diagonal coefficient $L_{qp}$ is obtained as $q^{eq} D_p/l$. In addition, another non-diagonal coefficient $L_{pq}$ brings the same form with $L_{qp}$ via the agreement $\chi_q = T \chi_p$ in fig. 4(b), where $\chi_p \equiv J_p/\Delta T$ for small $\Delta T$ with $f = 0$. We can rewrite the reciprocity coefficients as $L_{qp} = L_{pq} = q^{eq} \kappa^{eq}/l^2$ using the rate constant $\kappa^{eq}$ for the barrier-overcoming process of the stepwise motion in equilibrium, where $D_p = \kappa^{eq}/l^2$. This form clearly demonstrates that the characteristic heat brought by the barrier-overcoming process results in the reciprocity coefficients.
Fig. 4 – (a) Replot of the data in fig. 2(b). Both data for $T = 0.05$ and 0.033 are scaled to the same form as $J_q \simeq q^{eq} J_p / l$, which corresponds to $q_c \simeq q^{eq}$. $J_q$ and $J_p$ are calculated for $f \neq 0$, while $q^{eq}$ is evaluated for $f = 0$. (b) The agreement of $\chi_q$ with $\mu q^{eq}/l$ over various $K_c$. $T = 0.05$. $\chi_q \equiv J_q / f$ and $\mu \equiv J_p / f$ for small values of $f$ with $\Delta T = 0$. $q^{eq}$ is evaluated for $f = 0$ and $\Delta T = 0$. At the same time $T \chi_p$ is plotted, where $\chi_p \equiv J_p / \Delta T$ for small values of $\Delta T$ with $f = 0$. The observed equality $\chi_q = T \chi_p$ indicates that the reciprocity relation $L_{qp} = L_{pq}$ holds.

**Generality of the form for reciprocity coefficients.** – In this section, we show that expressions (6) of the reciprocity coefficients are valid in a class of Feynman’s ratchet attached to two heat baths. In this class of systems, we can generally define the particle flow $J_p$ and heat flow $J_q$ between the two baths and those temporal quantities $\dot{x}_p(t)$ and $\dot{J}_q(t)$. The reciprocity coefficients are written with the time correlation function in equilibrium states [11] as

$$L_{pq} = L_{qp} = \lim_{t_0 \to \infty} \frac{1}{2t_0} \int_{-t_0}^{t_0} dt \int_{-\infty}^{\infty} dt' \langle \dot{x}_p(t) \dot{J}_q(t + t') \rangle,$$

where $\langle \cdot \rangle$ denotes ensemble average. Nonvanishing contribution in the r.h.s. of eq. (8) comes from the stepwise motion of the particle. Supposing that the correlation decays within a finite time and that each stepwise motion is sufficiently separated in time, eq. (8) is rewritten as a summation of the contribution from each stepwise motion at $t = t_{i_s}$ as

$$\lim_{t_0 \to \infty} \frac{1}{2t_0} \sum_{\{i_s \mid t_{i_s} \in (0, t_0)\}} \int_{t_{i_s} - \tau}^{t_{i_s} + \tau} dt \langle \dot{x}_p(t) \int_{-\tau}^{\tau} dt' \dot{J}_q(t + t') \rangle,$$

where $i_s$ is the index of the stepwise motion and $\tau$ is a time sufficiently longer than the correlation time. Because the integration $\dot{q}_{i_s} \equiv \int_{-\tau}^{\tau} dt' \dot{J}_q(t + t')$ has no explicit dependence on $t$, the integration of $\dot{x}_p$ with $t$ can be done separately, which gives $+l$ and $-l$ for rightward and leftward stepwise motion, respectively. Classifying the stepwise motion indexed by $i_s$ into the rightward one indexed by $i_R$ and the leftward one indexed by $i_L$, eq. (9) gives

$$L_{pq} = \lim_{t_0 \to \infty} \frac{l}{2t_0} \left( \sum_{\{i_R \mid t_{i_R} \in (0, t_0)\}} \langle \dot{q}_{i_R} \rangle - \sum_{\{i_L \mid t_{i_L} \in (0, t_0)\}} \langle \dot{q}_{i_L} \rangle \right) - \frac{l}{2} \left( \kappa_R \langle \dot{q}_{i_R} \rangle - \kappa_L \langle \dot{q}_{i_L} \rangle \right) = q^{eq} K^{eq} l,$$

where $\langle \dot{q}_{i_R} \rangle = q_R = q^{eq}$ and $\langle \dot{q}_{i_L} \rangle = q_L = -q^{eq}$ [10]. $\kappa_R$ and $\kappa_L$ are rate constants for the rightward and the leftward stepwise motion, respectively, and in equilibrium $\kappa_R = \kappa_L = K^{eq}$. The expression of $L_{pq}$ in eq. (10) is equivalent to eq. (6). Furthermore, direct numerical calculations of the time integral of eq. (8) shows a good agreement with $q^{eq} D_p / l$ (data not shown).
Qualification of the heat pump. – A system functions as a heat pump if it can absorb energy from a cooler heat bath and dissipate it to a hotter one. The present system can function as a heat pump when the conditions

\[ \Delta T J_q \leq 0, \quad |J_q| \geq \hat{W}/2 \geq 0 \]  

are valid. The former inequality means that the heat flow \( J_q \) between the two heat baths is against temperature gradient \( \Delta T \). The latter means that energy is absorbed from one of the heat bath while dissipated to the other, \( i.e., J_1 J_2 \leq 0 \) where \( J_1 = -J_q - \hat{W}/2 \) and \( J_2 = J_q - \hat{W}/2 \).

For the linear response region with small \( f \) and \( \Delta T \), conditions (11) are reduced to

\[ \Delta T (\Delta T + \mu q^{eq} f/\lambda l) \leq 0, \]

which is satisfied in the light shaded area in the \( f-\Delta T \) plane of fig. 5. Here we substituted \( J_q \) of eqs. (5) and (6) into the first inequality of (11). \( \hat{W} \) is vanishing in the linear order of \( f \) and \( \Delta T \) because \( \hat{W} = J_p f \), which means that the second inequality in (11) always holds.

For larger values of \( f \) and \( \Delta T \), nonlinear effects (\( e.g., \) nonvanishing \( \hat{W} \)) are not negligible and the region where the system can work as a heat pump is reduced. For instance, for large values of \( f \) with \( \Delta T = 0 \), we obtain \( J_1 < 0 \) and \( J_2 < 0 \) as is seen in fig. 2(a) although eq. (12) is satisfied. The region of \( f \) and \( \Delta T \) satisfying the conditions (11) where the system actually functions as a heat pump are numerically identified in the model of fig. 1(a) as the dark shaded area in fig. 5. Adjusting the strength of the applied force within this confined area of parameters, we can choose the energy absorption rate from a cooler heat bath. The rate is maximum at \( |f| \approx |q^{eq}|/l \) in the present system (refer fig. 5)(2). The direction of the heat transfer can also be controlled by the direction of the applied force. The rightward mechanical force induces the absorption of heat from \( B_2 \) and the dissipation to \( B_1 \) (\( i.e., J_1 \leq 0 \) and \( J_2 \geq 0 \)), and vice versa for the leftward force (\( J_1 \geq 0 \) and \( J_2 \leq 0 \)).

With this heat pump, we can cool an object to the temperature limited by the conditions (11) optimizing the applied force. If we need to achieve lower temperature, we should construct a proper structure combining multiple pumps.

(2) In the present model, eq. (5) and \( \hat{W} = J_p f \) give a good estimation of \( J_1 \) and \( J_2 \), which result in maximum energy absorption rate from a cooler heat bath at \( |f| = |q^{eq}|/l(1 + |\Delta T|/2T) \approx |q^{eq}|/l = L_{qp}/L_{pp} \).
Discussion. – In this paper, we have shown that heat transfer can be controlled by a mechanical force. We clarified the conditions for the mesoscopic system to function as a heat pump based on the study of the linear response regime and numerical simulations in fully nonequilibrium. These results are consistent with the results obtained in a discretized solvable model for Feynman’s ratchet [4]. The Langevin dynamics adopted in this study suggests an intuitive picture based on the barrier-overcoming processes and associated heat transfer $q^{eq}$.

The form of the reciprocity coefficients in eq. (10) generally applies to the class of systems with an asymmetric periodic structure and two heat baths. When the direct measurement of $q^{eq}$ is difficult, we can estimate $q^{eq}$ from the Onsager coefficients as $q^{eq}/l = L_{qp}/L_{pp}$. This estimation can be applied to other models of heat pump, e.g. [4] and [12].

The form of the reciprocity coefficient $L_{qp} = q^{eq} \kappa^{eq} l$ implies that the present heat pump works effectively in small energy scales where barrier-overcoming processes are governed by thermal fluctuations. This is typically realized in molecular scales. The pump is not efficient in very low temperatures where the barrier-overcoming event rarely occurs. It would also be less effective for very high temperatures. This is because the value of $q^{eq}$, which depends on the left-right asymmetry of the system, would be smaller in higher temperatures.

Additional remark: After the completion of the present work, [13] and [14] were published and [12] appeared in the archive, where different models of heat pump are discussed.

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