

Reciprocating Motion on the Nanoscale[†]Yu. A. Makhnovskii,^{‡,§} V. M. Rozenbaum,^{*,‡,||,⊥} D.-Y. Yang,[‡] and S. H. Lin[‡]

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This paper analyzes the confined motion of a Brownian particle fluctuating between two conformational states with different potential profiles and different position-dependent rate constants of the transitions, the fluctuations arising from both thermal (equilibrium) and external (nonequilibrium) noise. The model illustrates a mechanism to transduce, on the nanoscale, the energy of nonequilibrium fluctuations into mechanical energy of reciprocating motion. Expressions for the reciprocating velocity and the efficiency of energy conversion are derived. These expressions are treated in more detail in the slow-fluctuation (quasi-equilibrium) regime, by simple perturbation theory arguments, and in the fast fluctuation limit, in terms of the potential of mean force. A notable observation is that the generalized driving force of the reciprocating motion is caused by two sources: the energy contribution due to the difference between the potential profiles of the states and the entropic contribution due to the difference between the position-dependent rate constants. Two illustrative examples are presented, where one of the two sources can be ignored and an exact solution is allowed. Among other aspects, we also discuss the ways to construct a molecular motor based on the reciprocating engine.

I. Introduction

The emergence of directed motion in small-scale systems due to nonequilibrium fluctuations, without any macroscopic gradients, has attracted considerable attention in recent years.^{1,2} The main motivation comes from molecular biology, especially from the challenge of understanding the operation mechanisms of the molecular motors and ion pumps,³ and nanoscale machinery, where there exists the problem of the fed energy transformation into directed motion of the microscopic engine.⁴ In this class of research, the emphasis is put on *directed* transport generation due to rectification of random fluctuations in spatially periodic systems with broken reflection symmetry. There exists, however, an alternative way suggested by analogy with macroscopic combustion motors: first to convert nonequilibrium fluctuations induced by a chemical reaction or any other external process into *reciprocating* mechanical motion (on long time and length scales compared with the microscopic ones) and then to rectify the reciprocating motion by a symmetry-breaking mechanism. It is worth mentioning that the concept of the reciprocating motion on the nanoscale, being quite general, is of interest by itself and appears to be relevant to treatment of the optomechanical conversion in a single-molecule device,⁵ a futile cycle in biochemistry,⁶ particle separation studies,⁷ strategy for molecular motor design,⁸ and in many other contexts.

A model of a nanoscale reciprocating engine has recently been developed by the present authors⁹ in terms of the confined

motion of a Brownian particle fluctuating between two (conformational) states with different spatially separated potential profiles. An obvious shortcoming of the model is that the dynamics for switching between states was assumed independent of particle spatial position and thermal noise. Hence, the results and the conclusions of ref 9 are only applicable to nanosystems switchable by extremely large (on the nanoscale) forces. In addition, as emphasized in ref 10, for any model of energy conversion on the nanoscale to be biologically relevant, the spatial dependence of the system's chemical activity should be incorporated into the model.

In this paper, we generalize the previously suggested model of a "nanoreciprocator"⁹ by taking into account the position dependence of the transition rate constants. The present strategy is more adequate for small-scale systems because the effect of inevitable (on this scale) thermal noise is given proper weight not only for spatial motion but also for the transitions between the competing states. In Section II, we formulate the model and derive the general equations for the reciprocating dynamics in the steady-state regime. At equilibrium, the detailed balance condition rules out the emergence of directed motion in either state, as one would expect. Nonequilibrium fluctuations brought about by a chemical reaction or any other external process break the detailed balance. So, the reciprocating motion "out of noisy states"¹¹ arises due to a nonthermal part of the noise. The external source supplies some energy to the system, part of which is transformed to the reciprocating motion. In Section III, the energetic aspects of the problem are analyzed. By introducing an effective chemical potential, we consider the efficiency of the input energy transformation into the energy of bidirectional mechanical motion and the mechanisms of dissipation. Section IV treats a more physically transparent picture that emerges in the limiting cases of fast and slow

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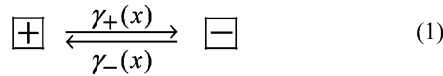
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transitions, where approximated analytical solutions are available under sufficiently general conditions.

From these results, it follows that there are two mechanisms causing the reciprocating motion: (i) an *energetic* mechanism (power-stroke model), in which the energy fed into the system in each flip from one state to the other is transformed into the potential energy of the particle and then used to push the particle forward or back upon relaxation; (ii) an *information* mechanism, in which the nonequilibrium noise acts as a source or sink of negentropy (physical information). The first implies different spatially separated potential profiles of the states, while the second emphasizes the key role of the position dependence of the rate constants for the interstate transitions. These mechanisms are discussed in Section V, where in particular, we show, with two simple exactly solvable examples, how the potential fluctuations and the entropic factor by themselves provide the operation of the nanoengine. The thermal noise is recognized as a necessary ingredient of the information mechanism, while in the energetic engine, it manifests itself only due to nonlinear effects. Finally, our concluding remarks are given in Section VI, where we focus on how the reciprocating nanoengine can be used for directed motion generation.

II. The Model and the Reciprocating Dynamics

We consider a Brownian particle moving in one dimension in a thermal bath at temperature T . The state of the particle is characterized by its spatial coordinate x and conformational variable σ . The particle is allowed to jump between two conformations, $\sigma = +$ and $\sigma = -$. The interstate switching dynamics is described by the rate equation



with the position-dependent transition rate constants $\gamma_{+}(x)$ and $\gamma_{-}(x)$. We assume that

$$\gamma_{\pm}(x) = \gamma_{\pm}^0(x) + \omega_{\pm}(x) \quad (2)$$

where $\gamma_{\pm}^0(x)$ are the rate constants for the transitions caused by equilibrium (thermal) fluctuations and $\omega_{\pm}(x)$ represent the external (nonthermal) noise.¹² The conformational variable σ specifies not only the transition rate constant $\gamma_{\sigma}(x)$ but also the potential profile $U_{\sigma}(x)$ and the particle friction coefficient ζ_{σ} . The potential profiles $U_{+}(x)$ and $U_{-}(x)$ are spatially separated and may have various shapes (e.g., be multiwelled but without infinitely deep wells). They are assumed to tend to infinity for $|x| \rightarrow \infty$ or to be defined in a finite domain with reflecting boundary conditions. In the latter case, $A < x < B$, infinite integration limits are replaced by the bounds A and B in all the formulas below that involve integration over x .

The dynamics of the model in the overdamped regime is governed by the master equations for the time evolution of probability densities $\rho_{\sigma}(x, t)$, $\sigma = +, -$, for finding the particle in state σ near point x at time t

$$\frac{\partial \rho_{\sigma}(x, t)}{\partial t} = -\frac{\partial}{\partial x} J_{\sigma}(x, t) - \sigma r(x, t) \quad (3)$$

with $r(x, t)$ as the net transition current density from state $+$ to $-$ at point x and time t ,

$$r(x, t) = \gamma_{+}(x)\rho_{+}(x, t) - \gamma_{-}(x)\rho_{-}(x, t) \quad (4)$$

and $J_{\sigma}(x, t)$ as the probability current in state σ at point x and

time t , which can be written as

$$J_{\sigma}(x, t) = -\zeta_{\sigma}^{-1} \rho_{\sigma}(x, t) \frac{\partial}{\partial x} \mu_{\sigma}(x, t) \quad (5)$$

The chemical potential for a species σ is given by

$$\mu_{\sigma}(x, t) = \mu_{\sigma}^0 + U_{\sigma}(x) + k_B T \ln \rho_{\sigma}(x, t) \quad (6)$$

where the position-independent term $\mu_{\sigma}^0 = \mu_{\sigma}^0(T)$ (the so-called standard chemical potential) reflects the contribution of internal degrees of freedom, and k_B is the Boltzmann constant. The total probability of both states is conserved and normalized to unity

$$\int_{-\infty}^{\infty} [\rho_{+}(x, t) + \rho_{-}(x, t)] dx = 1 \quad (7)$$

and the probability currents $J_{\sigma}(x, t)$ must vanish at $x \rightarrow \pm\infty$, $J_{\sigma}(\pm\infty, t) = 0$. The quantity of interest is the particle velocity in each state defined as

$$v_{\sigma}(t) = \int_{-\infty}^{\infty} dx J_{\sigma}(x, t) \quad (8)$$

After transient effects have died out, the system approaches a steady state, with the probability being the function of position only. In this regime, the probability current in state σ , $J_{\sigma}(x)$, is related to the probability current density between states, $r(x)$, by

$$J_{\sigma}(x) = -\sigma \int_{-\infty}^{\infty} dy r(y), \quad \sigma = +, - \quad (9)$$

This relation, together with the reflecting boundary condition at $x = \infty$, $J_{\sigma}(\infty) = 0$, leads to the condition of integral balance:

$$\int_{-\infty}^{\infty} dx \gamma_{+}(x) \rho_{+}(x) = \int_{-\infty}^{\infty} dx \gamma_{-}(x) \rho_{-}(x) \quad (10)$$

By substituting eq 9 into eq 8, we arrive at the following expression for the velocity:

$$v_{\sigma} = \sigma \int_{-\infty}^{\infty} dx x r(x), \quad \sigma = +, - \quad (11)$$

In the absence of external forcing, $\omega_{\pm}(x) = 0$ for all x , the system is at equilibrium. The probability densities $\rho_{\pm}^0(x)$ obey the Boltzmann distribution

$$\rho_{\pm}^0(x) = \frac{e^{-\beta[\mu_{\pm}^0 + U_{\pm}(x)]}}{e^{-\beta\mu_{+}^0} \int_{-\infty}^{\infty} dx e^{-\beta U_{+}(x)} + e^{-\beta\mu_{-}^0} \int_{-\infty}^{\infty} dx e^{-\beta U_{-}(x)}} \quad (12)$$

with $\beta = (k_B T)^{-1}$, and the detailed balance holds

$$\gamma_{+}^0(x)\rho_{+}^0(x) = \gamma_{-}^0(x)\rho_{-}^0(x) \quad \text{for all } x \quad (13)$$

The condition of detailed balance implies $r(x) = 0$, $J_{\pm}(x) = 0$, and hence zero average velocity in each state (see eq 11). A chemical reaction (or another source of nonequilibrium fluctuations) induces additional transitions between the states breaking the detailed balance and, as a result, leads to a nonzero value of v_{\pm} . Thus the model under consideration generates *bidirectional* (reciprocating) motion transforming the energy that comes from the source of nonequilibrium. The particle moves back and forth with the same absolute value of the velocity $|v_{\pm}|$. This is why, from here on, we present only the expressions for $v_{+} \equiv$

v . The complete average, $(v_+ + v_-)$, is zero, and no net motion of the system is generated in average, as it must be for bounded motion.

In what follows, we use eq 11 to consider the properties of reciprocating motion caused by nonequilibrium fluctuations. For the sake of convenience and future references, we introduce here some notations and definitions. First note that the (relative) population of state σ ($\sigma = +, -$) is $\delta_\sigma = \int_{-\infty}^{\infty} \rho_\sigma(x) dx$. Evidently, $\delta_+ + \delta_- = 1$. Then introduce the normalized-to-unity probability density $p_\sigma(x)$ for the particle position distribution in state σ , which is related to the joint probability density $\rho_\sigma(x)$ by the equation $\rho_\sigma(x) = \delta_\sigma p_\sigma(x)$. It is convenient to define the average over the position distribution in state σ as $\langle \cdots \rangle_\sigma \equiv \int_{-\infty}^{\infty} \cdots p_\sigma(x) dx$. Using the normalization condition (eq 7) and the integral balance condition (eq 10), the state populations δ_\pm can be expressed in terms of the averaged position-dependent rate constants:

$$\delta_\pm = \frac{\langle \gamma_\mp \rangle_\mp}{\langle \gamma_+ \rangle_+ + \langle \gamma_- \rangle_-} = \Gamma / \langle \gamma_\pm \rangle_\pm \quad (14)$$

where Γ is the effective frequency of modulation, $\Gamma^{-1} \equiv \langle \gamma_+ \rangle_+^{-1} + \langle \gamma_- \rangle_-^{-1}$. With these notations and $\hat{\gamma}_\pm \equiv \gamma_\pm / \langle \gamma_\pm \rangle_\pm$, eq 11 for the velocity takes the form

$$v = \Gamma (\langle x \hat{\gamma}_+ \rangle_+ - \langle x \hat{\gamma}_- \rangle_-) \quad (15)$$

Another useful expression for the velocity (valid for any confining potentials defined on the infinite interval $-\infty < x < \infty$)¹³ follows from eqs 5 and 8:

$$v = -\xi_+^{-1} \delta_+ \langle U'_+ \rangle_+ = \xi_-^{-1} \delta_- \langle U'_- \rangle_- \quad (16)$$

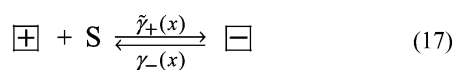
The second equality here reflects the fact that the total probability current in the system is zero. Note that v goes to zero when $\delta_\sigma \rightarrow 0$ or $\delta_\sigma \rightarrow 1$ so that the velocity exhibits a nonmonotonic behavior as a function of the state populations.

The main results of this section, eqs 15 and 16, generalize eqs 5 and 7 in ref 9 to the case of the position-dependent transition rate constants.

III. Energetics of Reciprocating Motion

When one deals with engines converting energy from a supplied to a desirable form, efficiency is an important measure of how successfully the engine accomplishes its task. On the nanoscale, the main difficulty of calculation of the efficiency (more precisely, the energy output) is related to the dual role of thermal fluctuations: they impel mechanical motion and, simultaneously, impede it. In this section, we discuss how the power output is defined in the case of the reciprocating engine under study.

We begin with the calculation of the free energy required for the operation of the engine. In so doing, we follow the way suggested in ref 14: the source of nonequilibrium fluctuations is represented by a nonuniform chemical potential expressed in terms of the parameters of the model. Consider, for clarity, a chemically driven motor with particles S (moving in the potential U_S with the friction coefficient ξ_S) serving as the “fuel”. Then the rate eq 1 describing the switching dynamics between states can be presented more generally:



At the steady state, the particles S are distributed with a

probability density $\rho_S(x)$ and the chemical potential of the fuel is given by

$$\mu_S(x) = \mu_S^0 + U_S(x) + k_B T \ln \rho_S(x) \quad (18)$$

The steady-state dynamics of the model is described by eq 3 (with $\partial \rho_\pm(x, t) / \partial t = 0$) supplemented by the equation

$$\frac{d}{dx} J_S(x) = -\gamma_+(x) \rho_+(x) + \gamma_-(x) \rho_-(x) = -r(x) \quad (19)$$

where $\gamma_+(x) = \tilde{\gamma}_+(x) \rho_S(x)$ is the pseudo-first-order rate coefficient (into which ρ_S has been incorporated), $r(x)$ is the reaction rate (see eq 4), and $J_S(x) = -\xi_S^{-1} \rho_S(x) d\mu_S(x)/dx$. The rate constants $\tilde{\gamma}_+$ and γ_- obey the detailed balance condition $\tilde{\gamma}_+ \rho_+^0 \rho_S^0 = \gamma_- \rho_-^0$, with the equilibrium probability densities $\rho_\pm^0(x)$ given by eq 12 and $\rho_S^0(x) = \exp[-\beta(\mu_S^0 + U_S(x))]$. Using this detailed balance condition, the chemical potential of the species S is expressible (in terms of the parameters of the model) in the physically suggestive form:

$$\mu_S(x) = \mu_-^0 - \mu_+^0 + U_-(x) - U_+(x) + k_B T \ln \frac{\gamma_+(x)}{\gamma_-(x)} = k_B T \ln \frac{1 + \omega_+(x)/\gamma_+^0(x)}{1 + \omega_-(x)/\gamma_-^0(x)} \quad (20)$$

In derivation of the second expression, we used eqs 2, 12, and 13. At equilibrium, $\omega_\pm(x) = 0$, the chemical potential $\mu_S(x)$ is zero, accounting for the fact that the species S do not disturb an equilibrium course of the reaction. Application of an external noise modulating the transition rate constants (at least one from ω_\pm is assumed nonzero) is equivalent to the free energy input from a nonequilibrium source with the chemical potential given by eq 20. When the system is driven out of equilibrium by imposing a nonequilibrium fuel concentration, the nonequilibrium chemical potential $\mu_S(x)$ determines the ratio $\gamma_+(x)/\gamma_-(x)$. In this paper, we consider another situation: spatial-dependent rate constants governing the transitions between the states, together with the potential profiles of the states, determine the chemical potential $\mu_S(x)$ of the effective fuel. Equation 20 suggests two mechanisms by which reciprocating motion occurs out of noisy states: the first (energetic) exploits the difference between the potential profiles of the states and the second (informational) mechanism takes advantage of the difference between the position-dependent rate constants. The energetic and informational mechanisms will be discussed in more detail in Section V.

The chemical potential $\mu_S(x)$ represents the free energy released as a result of “burning of the fuel” occurring at point x . Thus the free energy supplied per unit of time by the source of nonequilibrium reads:

$$P_{\text{in}} = \int_{-\infty}^{\infty} dx \mu_S(x) r(x) = \int_{-\infty}^{\infty} dx r(x) \left[U_-(x) - U_+(x) + k_B T \ln \frac{\gamma_+(x)}{\gamma_-(x)} \right] = k_B T \int_{-\infty}^{\infty} dx r(x) \ln \frac{1 + \omega_+(x)/\gamma_+^0(x)}{1 + \omega_-(x)/\gamma_-^0(x)} \quad (21)$$

Note that, in the steady state, the position-independent terms in the chemical potential do not contribute to P_{in} in view of the integral balance condition (10). It can be ascertained that $P_{\text{in}} \geq 0$, in accordance with the physical meaning of this quantity. Equations 20 and 21 clearly show that the input of the free energy required for the engine operation can be different from

the energy input. This can best be appreciated by looking at the case where the potential profiles of the states are the same and $\mu_s(x)$ does not depend on the potential at all. On the other hand, if $\omega_{\pm} \gg \gamma_{\pm}^0$ and, moreover, the quantities ω_{\pm} are position-independent (just as was the situation considered in ref 9), then P_{in} is determined solely by the energy input.

The entire energy consumed by the reciprocating engine is dissipated to the thermal environment as heat. We distinguish two mechanisms for the energy dissipation: the particle transitions between states resulting from the broken chemical equilibrium and the particle sliding within the potential profiles due to broken mechanical equilibrium. The former process is associated with the dissipated energy (per unit of time):

$$P_{\text{trans}} = \int_{-\infty}^{\infty} dx [\mu_s(x) + \mu_+(x) - \mu_-(x)] r(x) = k_B T \int_{-\infty}^{\infty} dx r(x) \ln \left[1 + \frac{r(x)}{\gamma_-(x) \rho_-(x)} \right] \quad (22)$$

The energy dissipation (per unit of time) corresponding to sliding within the potential profiles is given by

$$\begin{aligned} P_{\text{slid}} &= - \int_{-\infty}^{\infty} dx [\mu_+(x) - \mu_-(x)] r(x) = \\ &\quad - \int_{-\infty}^{\infty} dx \left[J_+(x) \frac{d\mu_+(x)}{dx} + J_-(x) \frac{d\mu_-(x)}{dx} \right] \\ &= \zeta_+ \int_{-\infty}^{\infty} \frac{J_+^2(x)}{\rho_+(x)} dx + \zeta_- \int_{-\infty}^{\infty} \frac{J_-^2(x)}{\rho_-(x)} dx = \frac{\zeta_+}{\delta_+} \langle v_+^2(x) \rangle_+ + \\ &\quad \frac{\zeta_-}{\delta_-} \langle v_-^2(x) \rangle_- \quad (23) \end{aligned}$$

where $v_{\sigma}(x) = J_{\sigma}(x)/\rho_{\sigma}$ is the particle velocity at point x in state σ . Note that the integrands (and hence the integrals) in eqs 22 and 23 are positive, and $P_{\text{trans}} + P_{\text{slid}} = P_{\text{in}}$, in accordance with the energy conservation law.

The energy output is widely identified with the work done by an engine against an external load force.¹⁴ Such a definition provides a successful measure of efficiency for the systems designed to increase the potential of an external agent, but it implies no utilization of the free energy input at all for the systems without loads. Often, especially on the nanoscale, one deals with engines intended simply to convert the free energy input into mechanical motion rather than to pull loads. To characterize the energy conversion efficiency in these systems, some alternative definitions of what the energy output really is were suggested.^{15,16}

For the reciprocating engine considered in this paper, we are faced with just such a problem. The engine is designed to convert nonequilibrium fluctuations into reciprocating motion, and the introduction of a constant external load force is meaningless here. This is why, for our purposes, we essentially adopt a concept put forward by Derényi et al.,¹⁵ in which the energy output is identified with the minimum free energy input required to accomplish the same task as the engine under study.

There is nothing more necessary for the engine operation than the occurrence of the drift in each state, which is unavoidably related to the energy dissipation. This suggests use of eq 23 for P_{slid} , where the local velocities $v_{\pm}(x)$ are replaced by their averaged values $\pm v$ representing the drift velocities; with such a replacement, P_{slid} takes its minimum value (in view of the inequality $\langle v_{\sigma}^2(x) \rangle \geq \langle v_{\sigma}(x) \rangle^2 = v^2$), thus specifying the mini-

mum power input required to cause the reciprocating motion, i.e., the power output of the engine, P_{out} . As a result, we get

$$P_{\text{out}} = \zeta_{\text{eff}} v^2 \quad (24)$$

where the effective friction coefficient is given by $\zeta_{\text{eff}} = \zeta_+/\delta_+ + \zeta_-/\delta_-$. The state population δ_{σ} renormalizes the friction coefficients ζ_{σ} (see also eqs 16 and 23). Despite the effective friction coefficient, ζ_{eff} becomes infinitely large when $\delta_{\sigma} \rightarrow 0$ or $\delta_{\sigma} \rightarrow 1$, the power output vanishes with the velocity v in these limits.

The main results of this section, eqs 21 and 24, may serve as a basis to gain insight into energetic aspects of the reciprocating motion on the nanoscale. In particular, they elucidate the efficiency of the energy conversion η , defined as the ratio of P_{out} to P_{in} , $\eta = P_{\text{out}}/P_{\text{in}}$.

IV. Slow and Fast Fluctuation Limits

While the problem formulated above is too complicated to be solved analytically in the general case, explicit solutions for arbitrary potential profiles can be found if there exists a separation of time scales. These are the time scale relevant to interstate hopping and the time scale associated with local relaxation within the states. In this Section, we analyze two opposite regimes of slow and fast transitions between the states, where perturbation methods suffice due to the clear-cut separation of time scales.

Slow Transitions. Assume that thermally activated and externally driven transitions between the states represent the slow components of the system dynamics, while the relaxation within the states constitutes the fast part of the dynamics. Under these conditions, at the steady state, the system is close to a *local* equilibrium, in the sense that the particle distribution in state σ ($\sigma = +, -$) can be described, to a quite good approximation, by the equilibrium distribution in the potential U_{σ} ,

$$p_{\sigma}^0(x) = \frac{e^{-\beta U_{\sigma}(x)}}{\int_{-\infty}^{\infty} e^{-\beta U_{\sigma}(x)} dx} \quad (25)$$

still not necessarily implying the *total* equilibrium. Only without external forcing, the transitions rates $\gamma_{\pm}(x) = \gamma_{\pm}^0(x)$ for all x , and the state populations, eq 14, take their equilibrium values $\delta_{\pm}^0 = \langle \gamma_{\mp}^0 \rangle / (\langle \gamma_+^0 \rangle + \langle \gamma_-^0 \rangle)$. Thus, the detailed balance holds, $r(x) = 0$, and the total equilibrium is achieved, which suggests, in particular, a zero average velocity in either state. However, with a slow external driving, the transition rates and the state populations differ from their equilibrium values, so that the detailed balance is broken and a nonequilibrium steady state with a nonzero reciprocating velocity is set up, which can be treated in terms of the local equilibrium distributions given by eq 25.

First, consider the adiabatic limit in which the driving is slow compared to the thermally activated transitions (also sufficiently slow), i.e., assume that $\epsilon_{\pm} = \max[\epsilon_{\pm}(x) = \omega_{\pm}(x)/\langle \gamma_{\pm}^0(x) \rangle] \ll 1$ (here the average values $\langle \cdots \rangle_{\pm}^0$ imply the equilibrium distribution (eq 25)). In this case, the external modulation can be regarded as a small perturbation to the equilibrium situation, which plays a quantitatively limited but qualitatively important role. To first order in ϵ_{\pm} , eq 4 for the rate $r(x)$ and eq 15 for the velocity are reduced to

$$r_{\text{ad}}(x) \simeq \Gamma_0[(\epsilon_+(x)p_+^0(x) - \epsilon_-(x)p_-^0(x)) - (\langle\epsilon_+(x)\rangle_+ \hat{\gamma}_+(x)p_+^0(x) - \langle\epsilon_-(x)\rangle_- \hat{\gamma}_-(x)p_-^0(x))] \quad (26)$$

$$v \simeq \Gamma_0[(\langle x\epsilon_+(x)\rangle_+^0 - \langle x\epsilon_-(x)\rangle_-^0) - \langle x\hat{\gamma}_+(x)\rangle_+^0(\langle\epsilon_+(x)\rangle_+^0 - \langle\epsilon_-(x)\rangle_-^0)] \quad (27)$$

where $\Gamma_0^{-1} = (\langle\gamma_+^0\rangle_+^{-1} + \langle\gamma_-^0\rangle_-^{-1})$ and $\hat{\gamma}_\pm(x) = \gamma_\pm^0(x)/\langle\gamma_\pm^0\rangle_\pm^0$. Note that $\langle x\hat{\gamma}_+(x)\rangle_+^0 = \langle x\hat{\gamma}_-(x)\rangle_-^0$ and $\int_{-\infty}^{\infty} r_{\text{ad}}(x) dx = 0$, in agreement with the integral balance condition given by eq 10. The first term in square brackets in eqs 26 and 27 represents the effect of varying the transition rates, while the second term accounts for the state overpopulations (relative to the equilibrium values) induced by the external driving. As eq 27 shows, for given profiles of the potential and the spontaneous transition rate constants, the velocity v can be either negative or positive depending on the magnitude and spatial distribution of the external noise process. Thus, a current inversion can be achieved in this regime.

Discussing the energy conversion efficiency, we assume, for simplicity, that $\omega_+(x) = \omega$, i.e., $\epsilon_+(x) = \epsilon = \omega/\langle\gamma_+^0\rangle_+^0$, $\omega_-(x) = 0$, and $\zeta_+ = \zeta_- = \zeta$. Then it follows from eq 20 that $\mu_S(x) \simeq \epsilon kT/\hat{\gamma}_+(x) \ll k_B T$, thus suggesting that the system in the adiabatic limit is close to equilibrium. In this regime, to lowest order in ϵ , the expressions for the power input and output, eqs 21 and 24, are of the form: $P_{\text{in}} \simeq \epsilon^2 \Gamma_0 k_B T \xi_0$, where $\xi_0 = (\langle\hat{\gamma}_+^{-1}\rangle_+^0 - 1) > 0$ in view of a Jensen inequality for the harmonic mean,¹⁷ and $P_{\text{out}} \simeq \epsilon^2 \Gamma_0 \zeta (\langle\gamma_+^0\rangle_+^0 + \langle\gamma_-^0\rangle_-^0) L_{\text{ad}}^2$, where $L_{\text{ad}} = \langle x(1 - \hat{\gamma}_+(x))\rangle_+^0$. Thus, the efficiency in the adiabatic regime is estimated by

$$\eta_{\text{ad}} \simeq \frac{(\langle\gamma_+^0\rangle_+^0 + \langle\gamma_-^0\rangle_-^0) \zeta L_{\text{ad}}^2}{\xi_0 k_B T} \quad (28)$$

being independent of the small parameter ϵ . Nevertheless, $\eta_{\text{ad}} \ll 1$ because it is of the same order as the transition to intrastate relaxation rate ratio, which is assumed to be small.

Another limiting situation, the so-called semiadiabatic limit,¹⁸ arises when a barrier separating the conformational states is very high compared to $k_B T$. Then the thermally activated jump rates, γ_+^0 and γ_-^0 , vanish and the interstate transitions are caused only by large (on the nanoscale) external forces. The forcing is assumed sufficiently slow, so that the local equilibrium (see eq 25) holds to a good approximation. In this regime, the velocity, eq 15, can be written as

$$v_{\text{sad}} \simeq \Gamma_\omega L_{\text{sad}} \quad (29)$$

where the mean rate of modulation $\Gamma_\omega = \langle\omega_+\rangle_+^0 \langle\omega_-\rangle_-^0 / (\langle\omega_+\rangle_+^0 + \langle\omega_-\rangle_-^0)$ is the small parameter. The meaning of the characteristic length $L_{\text{sad}} = \langle x\omega_+\rangle_+^0 / \langle\omega_+\rangle_+^0 - \langle x\omega_-\rangle_-^0 / \langle\omega_-\rangle_-^0$ becomes particularly transparent and illuminating for the position-independent forcing. In this case, L_{sad} is the difference of the equilibrium positions in the potential profiles $U_+(x)$ and $U_-(x)$, $L_{\text{sad}} = \langle x\rangle_+^0 - \langle x\rangle_-^0$. If, for example, the potential profiles are the precise copies of each other shifted by a distance L , $U_+(x + L) = U_-(x)$, then $L_{\text{sad}} = L$. It is also noteworthy that in the semiadiabatic regime, the efficiency is small, $\eta_{\text{sad}} \sim \Gamma_\omega$, because here we have $P_{\text{in}} \sim \Gamma_\omega$ and $P_{\text{out}} \sim \Gamma_\omega^2$.

Fast Transitions. When the transition rate constants tend to infinity, $\gamma_\pm(x) \rightarrow \infty$ for all x (or at least for those at which the probability densities are not negligibly small), the particle jumps from one state to the other many times before being moved an appreciable distance along the axis x . This suggests that, in the

zero approximation in $\tau(x) = [\gamma_+(x) + \gamma_-(x)]^{-1}$, the joint probability densities $\rho_+(x)$ and $\rho_-(x)$ are factorized as follows:

$$\rho_+(x) = \alpha(x)Q(x), \quad \rho_-(x) = [1 - \alpha(x)]Q(x) \quad (30)$$

where $Q(x) = \rho_+(x) + \rho_-(x)$ is the marginal probability density of the position variable and $\alpha(x) = \gamma_-(x)\tau(x)$ is the conditional probability to find the particle in state $+$, given the particle is at point x . In this approximation, the system described by the rate eq 17 is at chemical equilibrium, $\mu_+(x) + \mu_S(x) = \mu_-(x)$, with the chemical potentials $\mu_\sigma(x)$ ($\sigma = +, -, S$) given by eqs 6 and 20. Using relations (eq 30), an equation for $Q(x)$ is derived with regard to the zero value of the total probability current at any point x , $J_+(x) + J_-(x) = 0$. In terms of the potential of mean force U_{mf} , as defined by

$$U'_{\text{mf}}(x) = \overline{U'(x)} - k_B T [\ln z(x)]' \quad (31)$$

this equation takes the form $Q'(x) + \beta U'_{\text{mf}}(x)Q(x) = 0$. Here we have introduced the following notations: $U'(x) = \tilde{\alpha}(x)U'_+(x) + [1 - \tilde{\alpha}(x)]U'_-(x)$, $\tilde{\alpha}(x) = \xi\alpha(x)z(x)$, $\xi = \zeta_- / (\xi_+ + \zeta_-)$, and $z^{-1} = \xi\alpha(x) + (1 - \xi)[1 - \alpha(x)]$. Thus, in the high transition rate limit, the local Boltzmann equilibrium in the potential of mean force is established:

$$Q(x) = \frac{e^{-\beta U_{\text{mf}}(x)}}{\int_{-\infty}^{\infty} e^{-\beta U_{\text{mf}}(x)} dx} \quad (32)$$

The reason for such an effect is that the system in this regime is not capable of tracking the potential modulations and actually feels the effective potential $U_{\text{mf}}(x)$. Note that, even for identical potential profiles of the states, $U_+(x) = U_-(x) = U(x)$, the potential of mean force is different from $U(x)$ provided α is position-dependent and $\zeta_+ \neq \zeta_-$.

With this approach, the probability current in state σ ($\sigma = +, -$) can be written as

$$J_\sigma(x) = \sigma \frac{\alpha(x)[1 - \alpha(x)]}{\zeta_- \alpha(x) + \zeta_+[1 - \alpha(x)]} \mu'_S(x)Q(x) \quad (33)$$

where the chemical potential of the effective fuel $\mu_S(x)$ is defined by eq 20. The velocity v_σ and the net transition current density (reaction rate) $r(x)$ are found as $v_\sigma = \int_{-\infty}^{\infty} J_\sigma(x) dx$ and $r(x) = -\sigma J'_\sigma(x)$ (see eqs 3 and 8). In particular, in agreement with eq 16, we arrive at

$$v = -\zeta_+^{-1} \int_{-\infty}^{\infty} \mu'_+(x)\alpha(x)Q(x) dx = -\delta_+ \zeta_+^{-1} \langle U'_+ \rangle_+ = \zeta_-^{-1} \delta_- \langle U'_- \rangle_- \quad (34)$$

where $\mu'_\pm(x) = -[1 - \tilde{\alpha}(x)]\mu'_S(x)$ and the state populations are given by $\delta_+ = \int_{-\infty}^{\infty} \alpha(x)Q(x) dx$ and $\delta_- = 1 - \delta_+$. Consequently, the power output of the engine P_{out} is calculated according to eq 24, with the velocity v specified by eq 34.

In the zero approximation in τ used here, the rate of dissipation corresponding to the transitions between states, P_{trans} , eq 22, vanishes because the system is at chemical equilibrium, $\mu_S(x) = \mu_-(x) - \mu_+(x)$. Therefore, the entire free energy consumed by the system, P_{in} , is dissipated solely due to the particle sliding within the potential profiles, i.e., $P_{\text{in}} = P_{\text{slid}}$, with P_{slid} given by eq 23. Thus, in the high switching rate limit, P_{in} defined by eq 21, reads:

$$P_{\text{in}} = \int_{-\infty}^{\infty} dx \frac{\alpha(x)[1 - \alpha(x)]}{\xi_- \alpha(x) + \xi_+[1 - \alpha(x)]} \mu_s^2(x) Q(x) = \frac{\xi_+}{\delta_+} \langle v_+^2(x) \rangle_+ + \frac{\xi_-}{\delta_-} \langle v_-^2(x) \rangle_- \quad (35)$$

with $v_o(x) = J_o(x)/p_o(x)$, $p_+(x) = \delta_+^{-1} \alpha(x) Q(x)$, and $p_-(x) = \delta_-^{-1} [1 - \alpha(x)] Q(x)$. In view of the inequality $\langle v_o^2(x) \rangle \geq \langle v_o(x) \rangle^2 = v^2$, the efficiency η is, of course, less than unity, but it can take rather high values (especially at low temperatures) because the only mechanism of dissipation is the particle sliding within the potential profiles. It should be stressed, however, that although the fast transition regime seems to be promising as to the energy conversion efficiency, the input white noise forcing in this regime is transformed into reciprocating motion on the micro- rather than on the nanoscale, which cannot be rectified and used.

When considering the fast-fluctuation regime, one has to distinguish two important limiting cases. If thermal fluctuations are much faster than the external noise, $\gamma_{\pm}^0(x) \gg \omega_{\pm}(x)$ [i.e., for all x where the particle can be found with not a negligibly small probability, $\gamma_{\pm}^0(x) \rightarrow \infty$, while the rates $\omega_{\pm}(x)$ are finite], the zero approximation of $\alpha(x)$ is $\alpha_0(x) = \phi_+(x)/[\phi_+(x) + \phi_-(x)]$, where $\phi_{\pm}(x) = \exp[-\beta(U_{\pm}(x) + \mu_{\pm}^0)]$. With $\alpha(x) = \alpha_0(x)$, the probability densities $\rho_+(x)$ and $\rho_-(x)$ obey the Boltzmann distribution (see eq 12); then currents and velocities in each state as well as P_{in} and P_{out} reduce to zero. Thus in the fast-transition regime, if the thermal part of the noise dominates, the external noise does not disturb the total equilibrium. In the opposite limiting case of the external noise faster than thermal fluctuations ($\omega_{\pm}(x) \rightarrow \infty$, while the rates $\gamma_{\pm}^0(x)$ are finite and can be neglected in the zero approximation), the quantity $\alpha(x)$ should be replaced by $\alpha_w(x) \equiv \omega_-(x)/[\omega_+(x) + \omega_-(x)]$ in all the equations above.

The zero-approximation results presented in this section clarify the main qualitative features of the engine operation in the fast fluctuation regime. One can find the next terms of the τ expansion using an approach similar to that suggested in ref 19 for the position-independent transition rates. Such a derivation is, however, beyond the scope of the present paper.

V. Discussion

We have demonstrated that the model under consideration generates reciprocating motion by transforming the energy that comes from the source of nonequilibrium fluctuations. The model represents a reciprocating engine on the nanoscale. The action of the engine is induced by a generalized force. The results obtained in the previous sections (in particular, eqs 15, 20, 21, and 31) show that the generalized force may be treated as the sum of two forces: one arising from the difference between the potential profiles of the competing states and the other stemming from the difference between the position-dependent rate constants of interstate transitions. This suggests two mechanisms responsible for the engine operation, with quite distinct physical origins and manifestations: (i) the *energetic* mechanism in which the energy fed into the system in each jump from one state to the other is transformed into the potential energy of the particle and then used to push the particle forward or back upon relaxation; (ii) the *information* mechanism in which the nonequilibrium noise acts as a source or sink of negentropy (physical information). The first is based mainly on mechanical nonequilibrium, while the second is associated mainly with chemical nonequilibrium.

It is worth mentioning that the concept of two mechanisms (energetic and information) underlying the fluctuation induced transport²⁰ has been often invoked for modeling molecular motors and pumps.³ The deterministically dominant energetic mechanism is usually discussed in the framework of the so-called power stroke model.²¹ The stochastically dominant information mechanism has been proposed in studies of transport properties in inhomogeneous systems, with the position-dependent diffusion coefficient (or temperature)^{10,22} and position-dependent mobility²³ (or friction²⁴). From a microscopic description of the environment in terms of harmonic oscillator bath, the nonequilibrium noise associated with these inhomogeneities represents the nonthermal part of the energy in the nonequilibrium bath (coupled to the system) and acts as a source (or sink) of negentropy.²⁵ So the information mechanism stands for “a concept of possibilities rather than forces”.²³

As prototypes to illustrate the physics of the motion-inducing mechanisms, we present two simple and exactly solvable examples, with emphasis on the role of the thermal noise.

Energetic Engine. Let the conformational states $+$ and $-$ be characterized by the parabolic potentials, $U_{\pm}(x) = \frac{1}{2} k_{\pm}(x - a_{\pm})^2$, where k_{\pm} and a_{\pm} are the curvatures and the locations of the potential well minima separated by the distance $L = a_+ - a_-$. We assume a barrier between the conformational states to be very high compared to $k_B T$. Then the thermally activated jump rate constants γ_+^0 and γ_-^0 vanish and the interstate transitions are caused only by the external forcing. Moreover, we assume that the rate constants of the forcing, ω_+ and ω_- , are position-independent. So the model represents the reciprocating engine driven solely by the energetic mechanism.⁹

For this energetic engine, it immediately follows from eq 16 that the reciprocating velocity is given by

$$v = \frac{\gamma^* L}{1 + \gamma_+ \xi_+/k_+ + \gamma_- \xi_-/k_-} \quad (36)$$

where $\gamma^* = \omega_+ \omega_- / (\omega_+ + \omega_-)$. Particularly noteworthy is that v is temperature-independent, which suggests no contribution to the reciprocating velocity from the thermal noise. As was demonstrated earlier,⁹ this is a signature of the parabolic potential involved: equilibrium and nonequilibrium fluctuations are not coupled. Moreover, the thermal noise can be ignored if and only if the potentials $U_+(x)$ and $U_-(x)$ are parabolic. Even small nonparabolicity of the confining potential leads to the coupling of the noises and to the temperature-dependent velocity. Thus, within the energetic mechanism, the thermal noise comes into play with nonlinear effects. In other words, this mechanism is not purely deterministic. The temperature influence on the velocity may be manifested differently depending on the potentials. In particular, the thermal noise can have a constructive effect enhancing the velocity for a judiciously chosen potential pair.²⁶

Information Engine. A paradigmatic model for understanding the information mechanism is provided by the following reduction of our basic model introduced in Section II. Assume that the potential profiles of the states are identical, i.e., $U_+(x) = U_-(x) = U(x)$, and the interstate transition rate constants are given by

$$\gamma_{\pm}(x) = \tilde{\gamma}_{1\pm} \delta(x - x_1) + \tilde{\gamma}_{2\pm} \delta(x - x_2) \quad (37)$$

where x_1 and $x_2 > x_1$ are the positions of the “active sites” in which (and only in which) the transitions between the states are allowed, and the constant $\tilde{\gamma}_{i\sigma}$ ($i = 1, 2$ and $\sigma = +, -$) is the product of a characteristic frequency and a localization length

typical of the active site in state σ near point x_i . This model is analogous to the “chemical Maxwell demon” introduced in ref 14. Note that the concept of localized transitions is a valuable feature of modeling biologically important processes.^{3,10}

If the relation $\tilde{\gamma}_{1+}/\tilde{\gamma}_{1-} = \tilde{\gamma}_{2+}/\tilde{\gamma}_{2-}$ holds, the system is at equilibrium, $\mu_S(x) = 0$, (see eq 20), implying no probability current in either state. If this relation is violated, the system is out of equilibrium, $\mu_S(x) \neq 0$, and the reciprocating motion occurs. The deviation from equilibrium caused by the nonthermal part of the noise is quantified by $\Delta_\gamma \equiv \tilde{\gamma}_{1-}\tilde{\gamma}_{2+} - \tilde{\gamma}_{1+}\tilde{\gamma}_{2-}$, which determines the direction and the magnitude of the process. The emergence of the motion admits a simple qualitative explanation. With this setup, one of the active sites may be considered as a donor (acceptor) of particles in, say, state $+$ ($-$). Accordingly, the other active site in this state serves as a particle acceptor (donor). As a result, the probability current arises in a certain direction in state $+$ and in the opposite direction in state $-$. Note that switching between states does not change the particle energy. The energy necessary for the engine operation is taken from the nonequilibrium thermal bath. The active sites work as sources and sinks of the information about the particle position. The particle converts this information into reciprocating motion.

The simple model formulated above allows an exact solution. The reciprocating velocity, eq 11, can be found by solving eq 3 with the corresponding boundary conditions. The result is

$$v = \frac{(x_2 - x_1)\Delta_\gamma}{[\tilde{\gamma}_1 e^{\beta U(x_2)} + \tilde{\gamma}_2 e^{\beta U(x_1)} + \tilde{\gamma}_1 \tilde{\gamma}_2 \int_{x_1}^{x_2} e^{\beta U(x)} dx] \int_{-\infty}^{\infty} e^{-\beta U(x)} dx} \quad (38)$$

where $\tilde{\gamma}_i \equiv \tilde{\gamma}_{i+} + \tilde{\gamma}_{i-}$, $i = 1, 2$. Equation 38 clearly indicates the role of the thermal noise in the information mechanism, which is significantly different from that we have seen for the energetic mechanism. At low temperatures ($\beta \rightarrow \infty$), the velocity rapidly (exponentially) decays to zero, emphasizing that the information engine cannot operate without the thermal noise (as well as without the nonthermal noise). At high temperatures ($\beta \rightarrow 0$), the velocity given by eq 38 shows a slow (algebraic) decay to zero with β , suggesting that the strong thermal noise essentially destroys the confinement effect of the potential. Thus, upon temperature variation, the velocity exhibits a nonmonotonic behavior which is a manifestation of the dual role played by the thermal noise in the information mechanism.

VI. Concluding Remarks

In the previous sections, we have proposed a nanoscale reciprocating engine and discussed the basic physics of the engine operation. The engine processes externally induced fluctuations and generates reciprocating mechanical motion. This can be viewed as the first step on the way to solving the problem of directed motion generation in small-scale systems from the energy supplied by an external source. The next step involves a design of a symmetry-breaking mechanism to rectify the reciprocating motion. A simple example of such a mechanism is provided by a Brownian particle motion along a surface generating a longitudinal periodic asymmetric potential, which essentially decays with distance from the surface. If the reciprocating motion direction were surface-normal, it would give rise to nonequilibrium fluctuations of the asymmetric surface potential. As a result, the surface-parallel motion would finally result via a common mechanism.¹ A similar effect also

occurs if a particle reciprocates along a one-dimensional track, as is the case with a dimer placed into an asymmetric periodic potential. The potential energy of the dimer is contributed by the term dependent both on dimer internal coordinate and the position of its center of mass, which also leads to directed motion. The reciprocating motion thus causes the fluctuations of the asymmetric periodic potential in the well-known flashing potential model.¹

In the examples above, the reciprocating motion is rectified by an asymmetric periodic (ratchet) potential. However, conversion of the reciprocating into directed motion is doable without a ratchet potential too. As shown in ref 9, one of the possible ways is based on a so-called protein friction mechanism^{27,28} (additional channel of dissipation due to continuous making and breaking of weak chemical bonds between the protein and the microtubule). It is easy to verify that, if one of the protein ends is able to interact with the microtubule, while the other not, the reciprocating motion of the protein ends leads to the directed motion of the protein provided that the protein contraction and stretching run on essentially different time scales.

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