Efficiency of Energy Transduction in a Molecular Chemical Engine

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A simple model of the two-state ratchet type is proposed for molecular chemical engines that convert chemical free energy into mechanical work and vice versa. The engine works by catalyzing a chemical reaction and turning a rotor. Analytical expressions are obtained for the dependences of rotation and reaction rates on the concentrations of reactant and product molecules, from which the performance of the engine is analyzed. In particular, the efficiency of energy transduction is discussed in some detail.

KEYWORDS: molecular chemical engine, molecular motor, ratchet, efficiency, mechanoochemical coupling

The F₁ motor (F₁-ATPase), which is one of biological molecular motors,¹ ² is a remarkable molecular machine. It works as a rotary motor when it catalyzes the hydrolysis of adenosine triphosphate (ATP) into adenosine diphosphate (ADP) and inorganic phosphate (Pi).³ ⁴ It can also generate (synthesize) ATP from ADP and Pi when its rotor is forced to rotate in the opposite direction;⁵ ⁶ this is analogous to a heat engine working as a heat pump. A molecular machine, like the F₁ motor, that can convert chemical energy into mechanical work and vice versa will be referred to as a molecular chemical engine; it operates as a motor if it produces motion out of chemical energy, whereas it works as a generator if it generates “fuel” molecules of high chemical potential from “waste” molecules of low chemical potential by consuming mechanical energy.

It has been recognized that certain fundamental features of biological molecular motors can be captured by “Brownian motor” or ratchet models in which the system undergoes Brownian motion on a potential surface that changes stochastically between two or more profiles corresponding to different chemical states; see, for example, refs. 7–11 for reviews. For example, simple two-state ratchet models have demonstrated how the Brownian motion can be rectified to produce directed motion,¹² ¹³ the dependence of the motor velocity on the concentration of the fuel molecule ATP have been analyzed with simple models¹⁴–¹⁶ and with an elaborate model;¹⁷ and the efficiency of energy transduction¹⁸ and other measures of efficiency¹⁹–²¹ have been discussed. Although the effects of the concentration of fuel molecule or the input free energy on the performance of molecular motors have been studied in previous investigations, little attention has been payed to the effects of waste molecules.

In this letter we propose a simple model for molecular chemical engines that explicitly takes into account the effects of both the reactant and product molecules. Our model is a variant of two-state ratchet models⁷ ⁸ ¹¹–¹³ in general, and is closely related with the one outlined by Astumian and Bier²² in particular. The main difference between our model and other two-state models worked out earlier lies in the physics associated with transitions between the states: in the present model a transition occurs when the engine binds or releases a fuel or waste molecule, whereas it occurs as a result of ATP hydrolysis or the reverse reaction in some versions¹⁴–¹⁶,¹⁸ of previous models; in another²² the transitions represents binding and unbinding of nucleotides, but the way how the nucleotide concentrations are related with the transition rates are different from ours. Analytic expressions will be obtained for the dependences of rotation and reaction rates of the engine on the concentrations of reactant and product molecules. By using these results, the efficiency of energy transduction is studied for both the cases of the engine operating as a motor and as a generator.

Our model engine has a rotor, whose rotational angle is denoted by θ. The conformation (structure) of the engine is assumed to change as θ is varied. The engine catalyzes a hypothetical chemical reaction A ⇌ B instead of more complicated reaction ATP ⇌ ADP + Pi taking place in biological molecular motors. The chemical potentials μA and μB of molecules A and B, respectively, in the isothermal-environment of temperature T are assumed to satisfy the condition Δμ ≡ μA − μB > 0; i.e., A is the fuel and B is the waste. The engine can bind at most one molecule A or B. For simplicity, the binding and dissociation of A or B are supposed to be possible only if θ is at a particular value θA or θB, respectively, with 0 < θA < θB < 2π, i.e., if the engine is in a particular conformation.

We adopt the following assumption²³ on the reaction taking place in the engine: the relaxation of the “reaction coordinate” describing this reaction is so quick that this coordinate is always in thermal equilibrium, and the forward (backward) reaction A → B (B → A) proceeds with certainty when θ is varied from θA to θB (θB to θA). This will allow us to define an effective potential V₁(θ) (it is actually a free energy²³,²⁴ of the engine when it carries a “ligand molecule,” which is A for θ ∼ θA and B for θ ∼ θB. (Alternatively, the effective potential V₁ may be reduced from more detailed models²⁵,²⁶ of the F₁ motor, for example.)

The engine is said to be in “state 1” or “state 0” depending, respectively, on whether it is occupied by a ligand molecule or not. Let V₀(θ) be the potential (free
energy) of the engine in state 0. Then the torque exerted on the rotor by the engine in state $j$ ($j = 0, 1$) is given by $-dV_j/d\theta$. In Fig. 1, an example of the pair of potentials $V_0$ and $V_1$ (which is partly motivated by the analysis of experiments on the F$_1$ motor) is shown, together with “pathways” (indicated by arrows) the engine can take. For simplicity, we assume that a large barrier of potential $V_1$ lies in the interval $\theta_B < \theta < \theta_A + 2\pi$ (mod $2\pi$) which cannot be surmounted by the rotor; we also assume that potential $V_0$ has a barrier, which may be large or small, in the interval $\theta_A < \theta < \theta_B$. If the latter barrier is so large that the dashed passes in Fig. 1 cannot be taken, a single forward revolution (increase in $\theta$ by $2\pi$) of the rotor is always accompanied by a single forward chemical reaction $A \rightarrow B$; if this is the case, it is said that the “mechanochemical coupling” of the engine is tight. Otherwise, it is loose.\(^{9,28}\)

A transition between states 0 and 1 occurs when the engine binds or releases a ligand molecule (vertical arrows in Fig. 1). Let $w_j(\theta)$ be the rate of transition from state $j$ to the other state at angle $\theta$ of the rotor. The assumption mentioned above that the binding and the dissociation occur at particular values of $\theta$ may be expressed as

$$w_j(\theta) = \omega_j^A \delta(\theta - \theta_A) + \omega_j^B \delta(\theta - \theta_B) \quad (j = 0, 1),$$  \hspace{1cm} (1)

where $\omega_j^A$ and $\omega_j^B$ are positive constants associated with binding ($j = 0$) and dissociation ($j = 1$) of molecules $A$ and $B$ (see Fig. 1), and $\delta(\theta)$ is the delta function. The use of the delta function is a mathematical idealization, which has been introduced by several authors\(^{8,14,15,19,29-31}\) to carry out various calculations analytically.

The condition of detailed balance requires\(^{24}\) the first equality in

$$\frac{\omega_0^A}{\omega_1^A} = \exp\left(\frac{\mu_A - \Delta V_A}{k_BT}\right) = \frac{n_\alpha}{n_\beta} \quad (\alpha = A, B)$$  \hspace{1cm} (2)

to hold, where $\alpha = A$ or $B$, $\Delta V_\alpha = V_1(\theta_\alpha) - V_0(\theta_\alpha)$, and $k_B$ is the Boltzmann constant. The second equality in eq. (2) comes from the fact that the concentration of molecule $\alpha$ is proportional to $\exp(\mu_\alpha/k_BT)$ ($n_\alpha^0$ is the value of $n_\alpha$ for which $\mu_\alpha = \Delta V_\alpha$), and the third equality defines the reduced concentration $\rho_\alpha$. The binding rate of molecule $\alpha$ will be assumed to be proportional to $\rho_\alpha$; this implies that the dissociation rate is independent of $\rho_\alpha$ due to eq. (2). Hence we have

$$\omega_0^\alpha = \kappa_\alpha \rho_\alpha, \quad \omega_1^\alpha = \kappa_\alpha \quad (\alpha = A, B)$$  \hspace{1cm} (3)

with some positive constant $\kappa_\alpha$.

We shall consider a situation in which a constant torque $L \geq 0$, opposing the forward rotation, is exerted on the rotor externally. If the rotor revolves forward, the engine does mechanical work against the load torque (it works as a motor). On the other hand, if it revolves backward and the backward reaction $B \rightarrow A$ takes place, the engine works as a generator.

The rotational motion of the rotor is supposed to be described by the Langevin equation in the overdamped limit.\(^{10}\) Then, the rotation rate $\nu$ [the average of $(d\theta/dt)/2\pi$] and the reaction rate $r$ (the difference of the average numbers of forward and backward reactions per unit time) may be calculated from the steady-state solution to the Smoluchowski (Fokker-Planck) equation

$$\frac{\partial P_j}{\partial t} + \frac{\partial}{\partial \theta} \left( \omega_{j-1} P_j - \omega_j P_{j+1} \right) = -w_j P_j + \omega_{j-1} P_{j-1} - \omega_{j+1} P_{j+1} \quad (j = 0, 1),$$  \hspace{1cm} (4)

associated with the Langevin equation, for the probability densities $P_j(\theta, t)$ of $\theta$ in state $j$ at time $t$. In eq. (4), $w_j$ is the transition rate given in eq. (1) and $J_j = -D_0(\partial P_j/\partial \theta) - (dV_j/d\theta + L)(P_j/\gamma)$ is the probability current density in state $j$ with $D_0 = k_B T/\gamma$ the diffusion coefficient associated with the free rotation of the rotor, and $\gamma$ the drag coefficient of the rotor. Provided that the steady-state solution $P_j(\theta) = P_j(\theta + 2\pi)$ is normalized in such a way that $\int_0^{2\pi} P_j(\theta) d\theta = 1$, we have $\nu = J_0 + J_1$ and $r = \omega_0^A P_0(\theta_A) - \omega_0^B P_1(\theta_A) = \omega_0^A P_0(\theta_B) - \omega_0^B P_1(\theta_B)$; note that $J_0$ is independent of $\theta$ in the steady state.

The steady-state solution can be obtained analytically\(^{8,14,15,19,29-31}\) for the Smoluchowski equation (4) with transition rates $w_j(\theta)$ given as sums of the delta functions. In the present model, in which the rate constants are given by eq. (3), the following results for $\nu$ and $r$ are obtained:

$$\frac{\nu}{D_0} = \frac{\rho_A - \rho_B - a}{c_0 + c_A \rho_A + c_B \rho_B + c_{AB} \rho_A \rho_B},$$  \hspace{1cm} (5)

$$\frac{r}{D_0} = -\frac{b_\rho \rho_A - \sigma b_\rho \rho_B}{c_0 + c_A \rho_A + c_B \rho_B + c_{AB} \rho_A \rho_B},$$  \hspace{1cm} (6)

where $\sigma = \exp[2\pi \rho A + \Delta V_A/k_BT]$, and $a$, $b$'s and $c$'s are dimensionless functions of load torque $L$ ($a$, $c_A$ and $c_B$ depend also on $\kappa_A/D_0$ and $\kappa_B/D_0$). Coefficients $a$, $b$'s and $c$'s are given by expressions, too complicated to be presented here, containing integrals of certain functions of $V_j(\theta) + L\theta$. A few properties of these coefficients should be mentioned: (i) $b$'s and $c$'s are positive; (ii) $a = 0$ and $b_A = b_B$ for $L = 0$; (iii) $a > 0$ and $b_A > b_B$ for $L > 0$; and (iv) $a \rightarrow 0$, $b_A \rightarrow 1$, and $b_B \rightarrow 1$ in the limit of large barrier of potential $V_0$. From the first two properties together with the definitions (2) of $\rho_A$ and $\rho_B$, we observe that $\nu > 0$ and $r > 0$ for $\Delta \mu > 0$ in the absence of load torque ($L = 0$), as one would expect.

![Fig. 1. Schematic representation of the present model for a molecular chemical engine: an example of a pair of potentials $V_0(\theta)$ and $V_1(\theta)$ in states 0 and 1, respectively, is shown together with possible pathways, indicated by arrows, which the engine can take. See the text for details.](https://example.com/fig1.png)
It is emphasized that the dependences of $\nu$ and $r$ on $\rho_A$ and $\rho_B$ given by eqs. (5) and (6) are quite general in that they are independent of potential profiles ($V_0$ and $V_1$), which affect only the values of coefficients ($\sigma$, $a$, $b$'s and $c$'s). We also note that both $\nu$ and $r$ depend on $\mu_A$ and $\mu_B$ separately, while in the two-state models for molecular motors worked out previously$^{14-16,18,22}$ (and a single-state model$^{32}$ proposed recently) the chemical potentials come into play only through the difference $\Delta \mu = \mu_A - \mu_B$ (or $\Delta \mu = \mu_{\text{ATP}} - \mu_\text{ADP} - \mu_\text{Pi}$ if the reaction $\text{ATP} \rightleftharpoons \text{ADP} + \text{Pi}$ is considered instead of $A \rightleftharpoons B$).

In what follows we discuss the properties of the engine extracted from eqs. (5) and (6) for a particular set of potentials $V_0$ and $V_1$. Here, for simplicity, we consider the piecewise linear functions shown in Fig. 1: the vertices of $V_0$ are located at $\theta = \theta_A$, $\theta_C$, and $\theta_B$ with $\theta_C$ satisfying $\theta_A < \theta_C < \theta_B$, and those of $V_1$ at $\theta = 0$, $\theta_A$, and $\theta_B$; the potential shapes are specified by parameters $\Phi_0 = V_0(\theta_C) - V_0(\theta_A)$, $W_0 = V_0(\theta_B) - V_0(\theta_A)$, $\Phi_1 = V_1(0) - V_1(\theta_B)$, and $W_1 = V_1(\theta_A) - V_1(\theta_B)$. $^{33}$

It can be shown that eqs. (5) and (6) are approximated by

$$\nu \approx r \approx D_0 \rho_A / (c_0 + c_A \rho_A + c_A B \rho_{ABP})$$  \hspace{1cm} (7)

in the absence of the load ($L = 0$) if $\exp (W_j/k_B T) \gg 1$ ($j = 0, 1$), $\exp [(W_0 - \Phi_0)/k_B T] \gg 1$, $\kappa_A/D_0$ is not too small, and $\rho_B$ is not too large. The dependence on the concentration $\rho_A$ of fuel molecule for a fixed $\rho_B$ in this expression agrees with the one known as the Michaelis-Menten equation, and such a dependence of the rotation and reaction rates on the ATP concentration was observed for the $F_1$ motor.$^{4-27}$ The dependence on $\rho_B$ predicted in eq. (7) may be observed for the $F_1$ motor as the dependence on the ADP concentration.

Examples of the dependences of $\nu$ and $r$ on $L$ are shown in Fig. 2. Both $\nu$ and $r$ decrease monotonically with increasing $L$. The rotation rate $\nu$ becomes zero at a certain value $L_0$ of $L$, and the reaction rate $r$ becomes zero at a somewhat larger value $L_1$ (see the upper inset of Fig. 2). Thus, the engine works as a motor for $0 \leq L < L_0$ and as a generator for $L > L_1$, whereas it wastes both the chemical and mechanical energies for $L_0 < L < L_1$. It is not difficult to see that $L_0 < \Delta \mu/2\pi < L_1$ from property (iii) mentioned above, and that both $L_0$ and $L_1$ tends to $\Delta \mu/2\pi$ (therefore the useless interval of $L$ vanishes) in the tight coupling limit $[\exp (-B_0/k_B T) \rightarrow 0]$ according to property (iv).

In the examples shown in Fig. 2, the mechanochemical coupling is almost tight ($\nu \approx r$) for small load. However, the difference between $\nu$ and $r$ becomes apparent (the coupling becomes looser) as $L$ is increased. This is because the effective barrier height $\Phi_0 - W_0 - L(\theta_B - \theta_C)$ of potential $V_0$ seen from the location $\theta = \theta_B$ decreases and hence the leftward dashed passes in Fig. 1 are taken more frequently for larger $L$.

The efficiency $\eta$ of energy transduction is defined as $\eta = 2\pi \nu / \Delta \mu$ for motor and $\eta = r / \Delta \mu / 2\pi L$ for generator.$^{18}$ These expressions may be written as

$$\eta = \chi \eta_0,$$  \hspace{1cm} (8)

where $\chi = \nu / r$ ($r / \nu$) is the “tightness” of mechanochemical coupling, and $\eta_0 = 2\pi L / \Delta \mu$ ($\Delta \mu / 2\pi L$) is the efficiency in the tight coupling limit for motor (generator). Note that larger $\chi$ indicates tighter mechanochemical coupling, and we have $\chi = 1$ in the tight coupling limit.

An example of $\eta$ as a function of $L$ is depicted in the lower inset of Fig. 2, where we observe that $\eta$ for motor (generator) has a maximum near the “stall” load $L_0$ ($L_1$). In the tight coupling limit, the maximum efficiency of $\eta_0 = 1$ is achieved at $L = \Delta \mu/2\pi \mp 0$ (the minus sign for motor and the plus sign for generator). In the case of loose coupling, the maximum value of $\eta$ tends to be larger for larger $\chi$. Since the tightness decreases with increasing $L$ as explained above, the maximum of $\eta$ for motor is larger than that for generator in this example.

The dependence of $\eta$ on $L$ and $\Delta \mu$ for a particular choice of $\rho_B$ is shown as a contour plot in Fig. 3. In
this example, the largest efficiencies of motor and generator are achieved in the condition $\Delta \mu \sim 2\pi L \sim 20k_B T$ far from equilibrium ($\Delta \mu = L = 0$); a similar observation was made for related models by Parmeggiani et al.\(^\text{18}\)

Note that, in the tight coupling limit, we have the maximum value of $\eta = 1$ on the diagonal line $\Delta \mu = 2\pi L$.

We have obtained qualitatively similar patterns of contour lines to the one shown in Fig. 3 for other choices of $\rho_B$, although the locations and the heights of the peaks change as $\rho_B$ is varied. Let $\eta_m(\rho_B)$ be the maximum value of $\eta$ obtained by adjusting $L$ and $\Delta \mu$ for a given $\rho_B$. Figure 4 shows $\eta_m$ as a function of $\rho_B$ for three choices of the barrier height $\Phi_0$ of potential $V_0$. It is noted that $\eta_m$ increases with $\rho_B$ for both motor and generator, and saturates to a certain value—the upper limit of efficiency achieved by the engine (characterized by $V_0(\theta)$, $V_1(\theta)$, $\kappa_A$, $\kappa_B$ and $D_0$).

The dependence of $\eta_m(\rho_B)$ on $\rho_B$ shown in Fig. 4 may be understood qualitatively as follows. Remember that larger $\eta_m$ is expected for larger tightness $\chi$ of mechanochemical coupling. As the the concentration $\rho_B$ of molecule $B$ is increased, the binding of molecule $B$ (transition from state 0 to state 1 at $\theta = \theta_B$) occurs more frequently, which in effect leads to the decrease in the chance of taking the leftward dashed passes in Fig. 1. Therefore, the tightness $\chi$ and hence $\eta_m$ will increase with $\rho_B$, which is consistent with what we see in Fig. 4. In the case of motor, the dissociation of molecule $B$ occurs more frequently than the binding, and the former is not affected by $\rho_B$, while the binding of molecule $B$ is essential for generator. This explains the stronger dependence of $\eta_m$ on $\rho_B$ for generator than for motor observed in Fig. 4.

It may be worth remarking that the present model may be viewed as a motor driven by ion-flow across a membrane:\(^{34,35}\) the transition at $\theta_A$ can be viewed as ion exchange with the outside of the membrane, and the one at $\theta_B$ as ion exchange with the inside; in this case only one chemical species is involved.

In summary, we have proposed a minimal model for molecular chemical engines that properly takes into account the effects of fuel and waste molecules. The model is simple enough to work out various properties of the engine such as the efficiency of energy transduction. The detailed analysis of the model, including the derivations of various results presented here, and its extensions to situations other than the rotary motor will be reported in future publications.

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33. Note that difference $\Delta V(\theta) \equiv V_1(\theta) - V_0(\theta)$ is not important—because it depends on an arbitrarily chosen (common) zero of $\mu_A$ and $\mu_B$ (adding a constant $\mu_0$ to $\mu_A$ and $\mu_B$ amounts to increase in $\Delta V(\theta)$ by $\mu_0$), while the transition rates depend on $\mu_A$ and $V_1$ only through $\mu_A - \Delta V(\theta_0)$, which are not affected by such a choice.

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