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Symmetry relations for trajectories of a Brownian motor

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A Brownian motor is a nanoscale or molecular device that combines the effects of thermal noise, spatial or temporal asymmetry, and directionless input energy to drive directed motion. Because of the input energy, Brownian motors function away from thermodynamic equilibrium and concepts such as linear response theory, fluctuation dissipation relations, and detailed balance do not apply. The *generalized* fluctuation-dissipation relation, however, states that even under strongly thermodynamically nonequilibrium conditions the ratio of the probability of a transition to the probability of the time reverse of that transition is the exponential of the change in the internal energy of the system due to the transition. Here, we derive an extension of the generalized fluctuation dissipation theorem for a Brownian motor for the ratio between the probability for the motor to take a forward step and the probability to take a backward step.

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A Brownian motor is a nanoscale or molecular device that combines the effects of thermal noise, spatial or temporal asymmetry, and directionless input energy to drive directed motion [1,2]. Many biological motile systems may be driven by Brownian motors, and chemists have been able to synthesize molecules that function as Brownian motors [3,4]. In solution, viscous drag and thermal noise dominate the inertial forces that drive macroscopic machines. Because of the strong viscous drag, the motion of such a Brownian motor is overdamped and in one dimension can be described by the simple equation [5]

$$R\dot{\alpha} - X = \epsilon(t), \tag{1}$$

where $\epsilon(t)$ is Gaussian noise with mean $\mu=0$ and variance $\sigma^2=2Rk_BT/dt$ and R is the coefficient of viscous friction. In the following (and in the rest of the paper) we use units where the thermal energy $k_BT=1$. The generalized force $X=X(\alpha,\psi(t))$ can be written as the gradient of a scalar potential $X=-\partial H/\partial\alpha$ where

$$H(\alpha,\psi(t)) = U(\alpha) + \psi(t)z(\alpha) \tag{2}$$

is the sum of an intrinsic potential due to chemical interactions and any external load and an external time-dependent forcing term that is the product of canonically conjugate intensive and extensive thermodynamic parameters $z(\alpha)$ and $\psi(t)$, respectively [6]. The conjugate parameters include, e.g., molecular volume and pressure, entropy and temperature, or dipole moment and field. The underlying system is typically spatially periodic (possibly with a homogeneous force or load F) so that $U(\alpha+L)=U(\alpha)+\Delta U$, where $\Delta U=FL$ and $z(\alpha+L)=z(\alpha)$.

For any fixed value of ψ detailed balance requires

$$\frac{P(\alpha_i+L,\mathcal{T}|\cdots|\alpha_i,0)}{P^{\dagger}(\alpha_i,\mathcal{T}|\cdots|\alpha_i+L,0)} = e^{-\Delta U}, \tag{3}$$

where $P(\alpha_i+L,\mathcal{T}|\cdots|\alpha_i,0)$ is the conditional probability density that a particle starting at position α_i at time 0 goes to position α_i+L at time $\mathcal{T}$ by the specific trajectory (sequence of positions and times), denoted by $\cdots$, and $P^{\dagger}(\alpha_i,\mathcal{T}|\cdots|\alpha_i+L,0)$ is the conditional probability to follow the reverse of that process. The ratio depends only on the difference in energy between the initial and final points. It further holds that

$$\frac{P(L,\mathcal{T}|0,0)}{P(0,\mathcal{T}|L,0)} = e^{-\Delta U}, \tag{4}$$

where the net probability $P(L,\mathcal{T}|0,0)=\int_0\cdots\int^L P(\alpha_i+L,\mathcal{T}|\cdots|\alpha_i,0)$ is the integral over all trajectories from (0,0) to $(L,\mathcal{T})$.

A time-dependent modulation $\psi(t)$ causes dissipation and breaks detailed balance, in which case Eqs. (3) and (4) do not hold. It is even possible to have

$$\frac{P(L,\mathcal{T}|0,0)}{P(0,\mathcal{T}|L,0)} > 1, \quad e^{-\Delta U} < 1, \tag{5}$$

where the external stimulus $\psi(t)$ provides energy to drive uphill motion [7,8].

The *generalized* fluctuation-dissipation theorem [9,10] states that even under strongly thermodynamically nonequilibrium conditions the ratio of the probability of a forward (F) transition to the probability of the *time reverse* (F_R) of that transition is the exponential of the change in the internal energy of the system due to the transition

$$\frac{P_F(L,\mathcal{T}|\cdots|0,0)}{P_{F_R}(0,-\mathcal{T}|\cdots|L,0)} = e^{W-\Delta U}, \tag{6}$$

where W is the work supplied to the system by the external modulation in the forward trajectory. We can derive an extension of the generalized fluctuation dissipation theorem for a Brownian motor to obtain the ratio between the probability for the motor to take a forward step and the probability to

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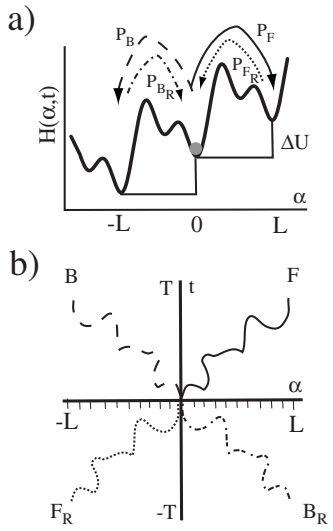


FIG. 1. Depiction of symmetry-related trajectories of a Brownian particle in a periodic ratchet potential. (a) Snapshot of a "ratchet" potential with a particle at $\alpha=0$. (b) With an external forcing $\psi(t)$ the four trajectories F, F_R, B, and B_R are distinct from one another.

take a backward step in *forward time*. First, we write Eq. (1) as a more rigorous finite-difference or update equation and convert to unit normal Gaussian noise $N(0,1)$ [11]:

$$\alpha_{i+1} - \alpha_i - R^{-1}X_{i+1}\Delta t = \sqrt{2R^{-1}\Delta t}N(0,1). \tag{7}$$

The time interval Δt is chosen to be sufficiently short that the change in position, $\Delta\alpha$, is very small. We used the relation $N(\mu,\sigma^2)=\mu+\sigma N(0,1)$ where $N(0,1)$ is a Gaussian random variable with zero mean and unit variance, the values n of which occur with probability $P(n)=\exp(-n^2/2)/(\sqrt{2\pi})$. Any two values of n are uncorrelated $\langle n_i n_k\rangle=\delta_{i,k}$.

Broken symmetry is an essential feature of a Brownian motor, so we split each of the position-dependent terms into even and odd components $U(\alpha)=U^{\mathrm{e}}(\alpha)+U^{\mathrm{o}}(\alpha)$ and $z(\alpha)=z^{\mathrm{e}}(\alpha)+z^{\mathrm{o}}(\alpha)$, where for any function $f^{\mathrm{e}}(-\alpha)=f^{\mathrm{e}}(\alpha)$ and $f^{\mathrm{o}}(-\alpha)=-f^{\mathrm{o}}(\alpha)$. Finite-difference expressions for the even and odd components of the generalized force, $X_{i+1}=X^{\mathrm{e}}_{i+1}+X^{\mathrm{o}}_{i+1}$, are

$$X^{(\mathrm{e,o})}_{i+1} = -\frac{\Delta U^{(\mathrm{o,e})}_{i+1} + \psi_{i+1}\Delta z^{(\mathrm{o,e})}_{i+1}}{\alpha_{i+1}-\alpha_i}, \tag{8}$$

where $\Delta f^k_{i+1}=f^k(\alpha_{i+1})-f^k(\alpha_i)$ for $f=U$, z and $k=\mathrm{e},\mathrm{o}$. For every forward trajectory $\{\alpha(t),\psi(t)\}$ with probability P_F, defined by

$$F \equiv 0 \overset{\psi_1}{\rightarrow} \alpha_1 \overset{\psi_2}{\rightarrow} \cdots \overset{\psi_{m-1}}{\rightarrow} \alpha_{m-1} \overset{\psi_m}{\rightarrow} L,$$

$$P_F = \prod_{i=0}^{M-1} P(\alpha_{i+1}|\alpha_i;\psi_{i+1}), \tag{9}$$

there are three symmetry-related trajectories, as seen in Fig. 1. One is a time-reverse trajectory [12] $\{\alpha(-t),\psi(-t)\}$ obtained by switching the sign of time $[t\rightarrow(\mathcal{T}-t)]$,

$$F_R \equiv 0 \overset{\psi_m}{\rightarrow} \alpha_{m-1} - L \overset{\psi_{m-1}}{\rightarrow} \cdots \overset{\psi_2}{\rightarrow} \alpha_1 - L \overset{\psi_1}{\rightarrow} -L,$$

$$P_{F_R} = \prod_{i=0}^{M-1} P(\alpha_i|\alpha_{i+1};\psi_{i+1}), \tag{10}$$

where we subtracted L from each position. Another is a backward trajectory $\{-\alpha(t),\psi(t)\}$ obtained by switching the sign of the position variable,

$$B \equiv 0 \overset{\psi_1}{\rightarrow} -\alpha_1 \overset{\psi_2}{\rightarrow} \cdots \overset{\psi_{m-1}}{\rightarrow} -\alpha_{m-1} \overset{\psi_m}{\rightarrow} -L,$$

$$P_B = \prod_{i=0}^{M-1} P(-\alpha_{i+1}|-\alpha_i;\psi_{i+1}). \tag{11}$$

The last is a backward reverse trajectory $\{-\alpha(t),\psi(-t)\}$ obtained by switching the sign of both time and of the position variable:

$$B_R \equiv 0 \overset{\psi_m}{\rightarrow} L-\alpha_{m-1} \overset{\psi_{m-1}}{\rightarrow} \cdots \overset{\psi_2}{\rightarrow} L-\alpha_1 \overset{\psi_1}{\rightarrow} L,$$

$$P_{B_R} = \prod_{i=0}^{M-1} P(-\alpha_i|-\alpha_{i+1};\psi_{i+1}), \tag{12}$$

where we added L to each position. Viewing Eq. (7) as a mapping between the "noise" space and "position" space [13], the conditional probability density given that the system is at position α_i after the ith step and that the value of the field is ψ_{i+1} for the $(i+1)$st step is seen to be

$$P(\alpha_{i+1}|\alpha_i,\psi_{i+1}) = \frac{e^{-(\Delta\alpha - R^{-1}X_{i+1}\Delta t)^2/4R^{-1}\Delta t}}{\sqrt{4\pi R^{-1}\Delta t}}, \tag{13}$$

where $\Delta\alpha=(\alpha_{i+1}-\alpha_i)$. The ratio of the probability density for the forward and time reverse steps is

$$\frac{P(\alpha_{i+1}|\alpha_i,\psi_{i+1})}{P(\alpha_i|\alpha_{i+1},\psi_{i+1})} = e^{X_{i+1}\Delta\alpha}, \tag{14}$$

and the ratio between the forward and time reverse trajectories is

$$\frac{P_F}{P_{F_R}} = \exp\left(\sum_{i=0}^{M-1} X_{i+1}\Delta\alpha\right) = e^{W_F-\Delta U}, \tag{15}$$

where

$$W_F = \sum_{i=0}^{M-1} \psi_{i+1}[\Delta z^{\mathrm{e}}(\alpha) + \Delta z^{\mathrm{o}}(\alpha)] \tag{16}$$

is the total external work done in the forward trajectory. Equation (15) is the generalized fluctuation dissipation relation [9,10], and the change in the internal energy of the system, $\Delta E=\Delta U-W_F$, is the dissipated work. The ratio of the probability density for a backward and backward time reverse is similarly obtained,

$$\frac{P_B}{P_{B_R}} = e^{W_B+\Delta U}, \tag{17}$$

where

$$W_B = \sum_{i=0}^{M-1} \psi_{i+1}[\Delta z^{\mathrm{e}}(\alpha) - \Delta z^{\mathrm{o}}(\alpha)] \tag{18}$$

is the total external work done in the backward trajectory. Finally, the ratio between a forward and backward steps is

$$\frac{P(\alpha_{i+1}|\alpha_i,\psi_{i+1})}{P(-\alpha_{i+1}|-\alpha_i,\psi_{i+1})} = e^{X^e_{i+1}\Delta\alpha - X^{\mathrm{e}}_{i+1}X^{\mathrm{o}}_{i+1}R^{-1}\Delta t}. \tag{19}$$

The ratio for the probability densities for a forward and backward trajectory follows immediately:

$$\frac{P_F}{P_B} = e^{-\Delta U}\exp\left(-\int_0^{\mathcal{T}} \frac{X^{\mathrm{e}}X^{\mathrm{o}}}{R}dt\right), \tag{20}$$

where we have taken the limit $\Delta t \to 0$ to get the integral form. Unlike the symmetry relations for the forward and reverse (and backward and backward reverse) trajectories, the ratio for the forward and backward trajectories involves the whole path. Equation (20) highlights the importance of broken symmetry—if either X^{o} or X^{e} is zero, the ratio of the probability for a forward step to a backward step is governed solely by the homogeneous force acting on the system and is independent of the work pumped in by the time-dependent modulation.

The results can be summarized using the Onsager-Machlup thermodynamic action [5,14]

$$\mathcal{S}_i = \frac{1}{4}\int_0^{\mathcal{T}} [\dot{\alpha}(t) + X_i/R]^2 dt,\ i = F,B,F_R,B_R, \tag{21}$$

where $X_{F,F_R} = X^{\mathrm{e}} + X^{\mathrm{o}}$ and $X_{B,B_R} = X^{\mathrm{e}} - X^{\mathrm{o}}$. Then

$$\frac{P_i}{P_j} = e^{R(\mathcal{S}_j - \mathcal{S}_i)}, \quad i,j = F,B,F_R,B_R. \tag{22}$$

The least action (optimal) trajectory is that for which the Lagrangian $\mathcal{L}(\alpha,\dot{\alpha}) = [\dot{\alpha}(t) + X_i/R]^2$ solves the Euler-Lagrange equation $[\partial/\partial\alpha - (d/dt)\partial/\partial\dot{\alpha}]\mathcal{L}(\alpha,\dot{\alpha}) = 0$. Systems where the trajectories that minimize the action in the forward and backward directions are mirror images of one another are "symmetric," while systems where these paths are not mirror images, but for which the least action is nonetheless the same in the forward and backward directions are "supersymmetric" [16]. Optimizing a Brownian motor requires that we design a system and modulation scheme that maximizes the difference between the least action in the forward and backward directions [17]. The relationship between the Onsager-Machlup approach and "fluctuation" theorems has been discussed recently [14,15].

We can most easily demonstrate application of these results in the context of a lattice model with only a few discrete states. Consider the standard ratchet potential [Fig. 1(a)] [2]

$$U(\alpha) = U_0\cos(2\alpha) + F\alpha,$$

$$z(\alpha) = z_0[\cos(s\pi)\cos(\alpha) + \sin(s\pi)\sin(\alpha)], \tag{23}$$

where the asymmetry parameter is $-1 \leqslant s \leqslant 1$. For $U_0 > \psi_0 z_0$, where ψ_0 is the amplitude of the external modulation, a single spatial period of the potential has two clearly defined energy wells, say 0 and 1. We can then describe the motion as a random walk on a lattice

$$\sim 0 \underset{\overleftarrow{k}_1}{\overset{\vec{k}_0}{\rightleftarrows}} 1 \underset{\overleftarrow{k}_0}{\overset{\vec{k}_1}{\rightleftarrows}} 0 \underset{\overleftarrow{k}_1}{\overset{\vec{k}_0}{\rightleftarrows}} 1 \underset{\overleftarrow{k}_0}{\overset{\vec{k}_1}{\rightleftarrows}} 0 \sim \tag{24}$$

The transition constants are

$$\vec{k}_0 = k[e^{-\Delta U}(\phi^{\mathrm{e}}\phi^{\mathrm{o}})]^{1/4},$$

$$\vec{k}_1 = k[e^{-\Delta U}/(\phi^{\mathrm{e}}\phi^{\mathrm{o}})]^{1/4},$$

$$\overleftarrow{k}_0 = k[e^{\Delta U}(\phi^{\mathrm{e}}/\phi^{\mathrm{o}})]^{1/4},$$

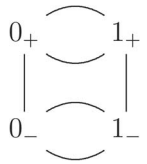
$$\overleftarrow{k}_1 = k[e^{\Delta U}(\phi^{\mathrm{o}}/\phi^{\mathrm{e}})]^{1/4}, \tag{25}$$

where $\phi^{\mathrm{e}} = \mathrm{e}^{4z_0\psi(t)\cos(s\pi)}$ and $\phi^{\mathrm{o}} = \mathrm{e}^{4z_0\psi(t)\sin(s\pi)}$. The even part of the time-dependent perturbation $\cos(s\pi)$ influences the relative energies of the two states 0 and 1, and the odd part of the time-dependent perturbation $\sin(s\pi)$ influences the relative heights of the two barriers. Irrespective of the value of s or of the form of $\psi(t)$, a corollary of detailed balance for rate processes

$$\frac{\vec{k}_0\vec{k}_1}{\overleftarrow{k}_0\overleftarrow{k}_1} = e^{-\Delta U} \tag{26}$$

holds at every instant. Nevertheless, any time-dependent modulation $\psi(t)$ drives motion to the right when $\Delta U = 0$ and can do work against a small nonzero $\Delta U > 0$. The infinitely extened lattice model can more conveniently be written as a cycle $0 \circlearrowleft 1$, where a clockwise transition indicates a half-step to the right and a counterclockwise transition indicates a half-step to the left on the lattice.

For the specific case that $\psi(t)$ is externally generated dichotomic noise $(+\Psi \overset{\gamma}{\rightleftarrows} -\Psi)$ in which $\psi(t)$ switches between $+\Psi$ and $-\Psi$ with a Poisson distributed random lifetime (average $1/\gamma$) the combined stepping and switching process can be described by a single diagram [6]

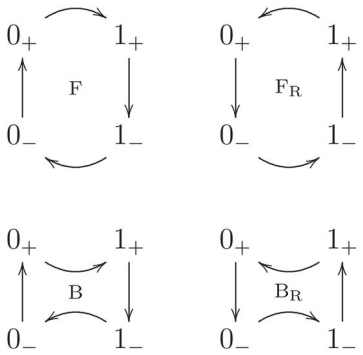


(27)

This case is particularly relevant for Brownian motors that are driven, e.g., by the stochastic binding of chemical fuel molecule [e.g., adenosine triphosphate (ATP)] and release of product [adensoine diphosphate (ADP)]. For such motors, the forward process (F) is one in which one ATP is converted into ADP and the motor takes one step forward; the forward reverse (F_R) process is one in which one ADP is converted into ATP and the motor takes one step back; the backward

process (B) is one in which one ATP is converted into ADP and the motor takes one step backward; and the backward reverse process (B_R) is one in which one ADP is converted into ATP and the motor takes one step forward.

The overall diagram can be broken into six cycles [6]—two cycles for the uncoupled stepping, one with fixed $+\Psi$ and the other with fixed $-\Psi$, two cycles for the dissipative back and forth motion with no net stepping, and two cycles describing net stepping coupled to the external fluctuation. The last two, coupled, cycles are of particular interest. The forward, reverse, backward, and backward reverse paths are



(28)

The probability for completion of a cycle is proportional to the product of the transition constants in the cycle. The proportionality constants involve rate constants for back and forth transitions, lifetimes of the states within the cycle, etc. Importantly, since F, F_R, B, and B_R directional cycles [Eq. (28)] involve the same states, the proportionality constants are the same for all of these symmetry-related cycles. Thus, with $k_{i_\pm}=k_i(\psi(t)=\pm\Psi)$, it is easy to derive

$$\frac{P_F}{P_{F_R}}=\frac{\vec{k}_{0_+}\vec{k}_{1_-}}{\overleftarrow{k}_{1_+}\overleftarrow{k}_{0_-}}=e^{W-\Delta U},$$

$$\frac{P_B}{P_{B_R}}=\frac{\overleftarrow{k}_{0_+}\overleftarrow{k}_{1_-}}{\vec{k}_{1_+}\vec{k}_{0_-}}=e^{W+\Delta U}, \tag{29}$$

where $W=\ln(\phi_+^{\mathrm{o}})$ is the work done in the forward cycle when the energy is increased by $2z_0\Psi\sin(s\pi)$ in going from $0,-\rightarrow 0,+$ and again from $1,+\rightarrow 1,-$. Here and below $\phi_+^{(\mathrm{e,o})}=\phi^{(\mathrm{e,o})}(\psi(t)=+\Psi)$. The ratio of the probabilities for a forward and backward cycle is

$$\frac{P_F}{P_B}=\frac{\vec{k}_{0_+}\vec{k}_{1_-}}{\overleftarrow{k}_{0_+}\overleftarrow{k}_{1_-}}=e^{-\Delta U}\phi_+^e, \tag{30}$$

and the ratio of the net forward to backward steps is

$$\frac{P_F+P_{B_R}}{P_B+P_{F_R}}=e^{-\Delta U}\left(\frac{1+\phi_+^{\mathrm{e}}\phi_+^{\mathrm{o}}}{\phi_+^{\mathrm{o}}+\phi_+^{\mathrm{e}}}\right). \tag{31}$$

The expansion of the coefficient in Eq. (31) involves only even powers of the amplitude ψ_0 of the external driving—the Brownian motor mechanism is a fundamentally nonlinear effect of the external driving [18]. Many recent synthetic implementations of molecular Brownian motors involve motion between discrete binding sites. Without an external driving the thermally activated transitions show no long-time order irrespective of structural asymmetry, consistenty with the principle of detailed balance. By using external energy to manipulate the environment, even in a seemingly random way, it is possible to break detailed balance and to drive directed motion. The symmetry relations derived here may provide insight into how it may be possible to optimize synthetic molecular motors.

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