Reciprocal Relations for Nonlinear Coupled Transport

R. Dean Astumian[*]
University of Maine, Orono, Maine, USA

(Received 8 February 2008; published 24 July 2008)

Reciprocal relations are derived for transport between two pairs of reservoirs energetically coupled at mesoscopic contact points through second order in the chemical potential differences. In the derivation attention is focussed on the average number of particles transported between the reservoirs during each excursion of the contact point away from, and regression back to, a steady state. All quantities involved are experimentally accessible in the full counting statistics of the transport processes.

DOI: 10.1103/PhysRevLett.101.046802 PACS numbers: 73.23.−b, 73.50.Fq

It has long been recognized [1] that symmetry relations such as those derived by Onsager [2,3] for irreversible processes are extremely useful for understanding transport mediated by small structures (mesoscopic regions) connecting several macroscopic reservoirs. Examples include physical devices such as coupled quantum dots and quantum point contacts [4,5], and also biological systems such as membrane transporters and ion pumps [6], coupled enzyme systems [7–9], and even biomolecular motors [10–12]. Near thermodynamic equilibrium the generalized transport currents J_i usually depend nearly linearly on the "thermodynamic forces" X_i,

$$\begin{aligned} J_1 &\approx L_{11}X_1 + L_{12}X_2 + \mathcal{O}(2), \\ J_2 &\approx L_{21}X_1 + L_{22}X_2 + \mathcal{O}(2). \end{aligned} \tag{1}$$

Onsager showed by very general arguments that the cross coupling coefficients are equal, $L_{12} = L_{21}$. Thus, for small forces, the magnitude of the flow J_1 caused by the force X_2 (with $X_1 = 0$) is identical to the magnitude of the flow J_2 caused by the force X_1 (with $X_2 = 0$) if the magnitude of X_2 in the former case is equal the magnitude of X_1 in the latter case. This reciprocity of the flows and forces does not hold for larger forces where higher order terms become important. Further, under some circumstances, $L_{12} = L_{21} \equiv 0$ by symmetry. It is still possible that the flows are coupled at higher order [13,14], but no general relationship describing the cross coupling has been given even for very small forces.

In this Letter I derive reciprocal relations between coefficient functions for transport through a mesoscopic conductor valid for arbitrary magnitude forces, and use these relations to derive explicit reciprocal relations between the constant condactances for transport through second order. I focus on the fluctuations of the mesoscopic region about its steady state and on the average number of particles transferred between the macroscopic reservoirs during each cyclic excursion away from, and regression back to, the steady state condition. This quantity is accessible in the full counting statistics [15] of the processes, and hence the predictions are open to experimental test.

Consider the system shown in Fig. 1. Particles move between a left reservoir $\mathcal{L}_1$ maintained at chemical potential $\mu_{\mathcal{L}_1}$ and a right reservoir $\mathcal{R}_1$ maintained at chemical potential $\mu_{\mathcal{R}_1}$ through a mesoscopic region $\mathcal{M}_1$ with an occupancy n_1. In a separate channel particles move between a left reservoir $\mathcal{L}_2$ maintained at chemical potential $\mu_{\mathcal{L}_2}$ and a right reservoir $\mathcal{R}_2$ maintained at chemical potential $\mu_{\mathcal{R}_2}$ through a mesoscopic region $\mathcal{M}_2$ with occupancy number n_2. These two transport processes are coupled by energetic interactions at the contiguous mesoscopic regions $\mathcal{M}_1$ and $\mathcal{M}_2$, but there is no mass transfer between the two channels.

After a sufficient time, the mesoscopic region reaches steady state occupancy $(n_{1,\mathrm{ss}}, n_{2,\mathrm{ss}})$ and the occupancies fluctuate around the steady state levels $n_1(t) = n_{1,\mathrm{ss}} + \delta n_1(t)$ and $n_2(t) = n_{2,\mathrm{ss}} + \delta n_2(t)$ where $\langle \delta n_1(t)\rangle = \langle \delta n_2(t)\rangle = 0$ (see Fig. 2). During each excursion away from, and regression back to, the steady state condition $(n_{1,\mathrm{ss}}, n_{2,\mathrm{ss}})$ an integer number N_1 of particles are transferred between reservoirs $\mathcal{L}_1$ and $\mathcal{R}_1$, and N_2 particles are transferred between reservoirs $\mathcal{L}_2$ and $\mathcal{R}_2$. The numbers N_1 and N_2 can be calculated by keeping track of whether each particle entering (right and up arrows) and leaving

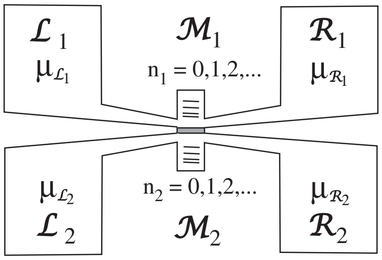

FIG. 1. Setup illustrating transport of particles between reservoirs $\mathcal{L}_1$ and $\mathcal{R}_1$ held at fixed chemical potentials $\mu_{\mathcal{L}_1}$ and $\mu_{\mathcal{R}_1}$, respectively, and between resorvoirs $\mathcal{L}_2$ and $\mathcal{R}_2$ held at fixed chemical potentials $\mu_{\mathcal{L}_2}$ and $\mu_{\mathcal{R}_2}$, respectively. The particles move through mesoscopic regions $\mathcal{M}_1$ and $\mathcal{M}_2$, the states of which are given by the discrete occupancies n_1 and n_2. Energy coupling but not mass transfer between the two channels can take place in the mesoscale region.

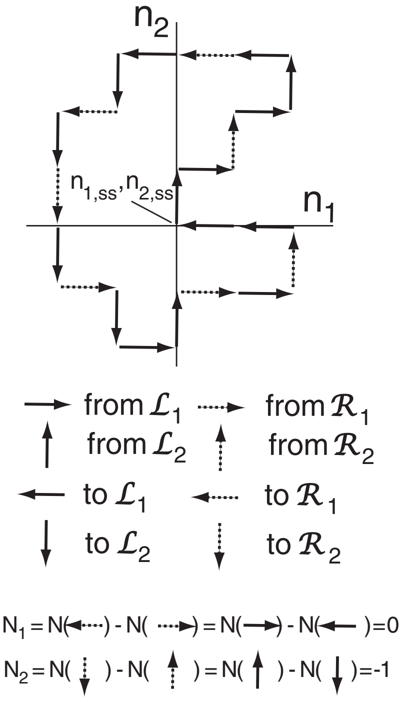

FIG. 2. Illustration of a trajectory away from, and regression back to, the steady state occupancy of the mesoscopic regions $\mathcal{M}_1$ and $\mathcal{M}_2$ shown in Fig. 1. I use solid arrows to indicate particles moving from or to the left reservoirs, and dotted arrows to indicate particles moving from or to the right reservoirs. Counting the arrows allows determination of the number of particles, N_1 and N_2 transferred between the macroscopic reservoirs in the excursion.

(left and down arrows) the mesoscopic region comes from the left (solid arrow) or right (dotted arrow) reservoir. By inverting the direction of each arrow in any trajectory one obtains the microscopic reverse of that trajectory. In this microscopic reverse trajectory the signs (but not magnitude) of both N_1 and N_2 are changed. The ratio of the probabilities for any such forward and microscopic reverse trajectories depends only on the changes brought about in the environment—i.e., on N_1, N_2, and on the chemical potential differences between the left and right macroscopic reservoirs $\Delta\mu_1 = \mu_{\mathcal{L}_1} - \mu_{\mathcal{R}_1}$, and $\Delta\mu_2 = \mu_{\mathcal{L}_2} - \mu_{\mathcal{R}_2}$. Thus, in units where the thermal energy $k_B T = 1$ with T the temperature of all baths, the ratio of the total probability for a trajectory that results in transport of N_1 and N_2 particles to the probability for a trajectory that results in transport of $-N_1$ and $-N_2$ particles is

$$\frac{P(N_1, N_2)}{P(-N_1, -N_2)} = e^{N_1\Delta\mu_1 + N_2\Delta\mu_2}. \tag{2}$$

Equation (2) follows from microscopic reversibility. Note that the ratio $P(N_1, N_2)/P(-N_1, N_2)$ is not thermodynamically constrained since a trajectory in which $-N_1$ and N_2 particles are transported is not the microscopic reverse of any trajectory in which N_1 and N_2 particles are transported. Indeed, the ratios $P(-N_1, N_2)/P(N_1, N_2)$ are the key quantitative descriptors of coupling between the transport processes in channels 1 and 2. The focus on completions of forward and reverse cycles of the occupancy of the mesoscopic region is reminiscent of the approach developed by Hill [8,16] for analyzing biological energy transduction in terms of the cycles of the proteins responsible for these conversion processes. A very elegant description of detailed balance for full counting statistics for a single transport process, and related symmetries, has been given recently by Tobiska and Nazarov [17].

The numbers of particles transferred between the left and right reservoirs in an excursion away from and back to the steady state, averaged over many excursions, are

$$\langle N_\alpha\rangle = \sum_{N_1=-\infty}^{+\infty}\sum_{N_2=-\infty}^{+\infty} N_\alpha P(N_1, N_2), \qquad \alpha = 1, 2. \tag{3}$$

Using Eq. (2) the averages in Eq. (3) can be rewritten,

$$\begin{aligned}\langle N_\alpha\rangle = &\sum_{N_\alpha=1}^{+\infty} N_\alpha P(N_\alpha, 0)(1 - e^{-N_\alpha\Delta\mu_\alpha})\\ &+ \sum_{N_1=1}^{+\infty}\sum_{N_2=1}^{+\infty} N_\alpha[P(N_1, N_2)(1 - e^{-N_1\Delta\mu_1 - N_2\Delta\mu_2})\\ &\mp P(-N_1, N_2)(1 - e^{+N_1\Delta\mu_1 - N_2\Delta\mu_2})], \quad \alpha = 1, 2,\end{aligned} \tag{4}$$

where I used $P(-N_1, N_2) = P(N_1, -N_2)e^{-N_1\Delta\mu_1 + N_2\Delta\mu_2}$ in the expression for $\langle N_1\rangle$ and, hence, take " $-$" for $\alpha = 1$ and " $+$" for $\alpha = 2$ in the symbol $\mp$ in the second line of Eq. (4). Expanding Eq. (4) in powers of $\Delta\mu_1$ and $\Delta\mu_2$ I write

$$\langle N_\alpha\rangle = \sum_{i=0}^{\infty}\frac{1}{i!}G_i^{(\alpha)}\Delta\mu_\alpha^i + \sum_{i=0}^{\infty}\sum_{j=1}^{\infty}\frac{1}{i!j!}G_{i,j}^{(\alpha)}\Delta\mu_\alpha^i\Delta\mu_{\text{not}\alpha}^j \tag{5}$$

where " notα" indicates 2 if $\alpha = 1$ and 1 if $\alpha = 2$. The first sum, $\sum_{i=0}^{\infty}\frac{1}{i!}G_i^{(\alpha)}\Delta\mu_\alpha^i \equiv \langle N_{\alpha,\text{d}}\rangle$, includes the direct terms—those that depend on $\Delta\mu_\alpha$ only. The "direct term" is zero when the direct force is zero, i.e., when $\langle N_{\alpha,\text{d}}\rangle = 0$ for $\Delta\mu_\alpha = 0$. The second sum, $\sum_{i=0}^{\infty}\sum_{j=1}^{\infty}\frac{1}{i!j!}G_{i,j}^{(\alpha)}\Delta\mu_\alpha^i\Delta\mu_{\text{not}\alpha}^j \equiv \langle N_{\alpha,\text{c}}\rangle$, includes the cross terms on which I focus in this Letter. In the expression $G_{i,j}^{(\alpha)}$ the superscript (α) indicates that the term appears in the equation for $\langle N_\alpha\rangle$, and the subscripts indicate that the coefficient multiplies $\Delta\mu_\alpha^i\Delta\mu_{\text{not}\alpha}^j$ in the expansion in powers of $\Delta\mu_1$ and $\Delta\mu_2$. The coefficients are

$$\begin{aligned}G_{i,j}^{(\alpha)} = &\sum_{N_1=0}^{+\infty}\sum_{N_2=0}^{+\infty} N_\alpha^{i+1}N_{\text{not}\alpha}^j[(-1)^{j+i+1}P(N_1, N_2)\\ &\pm (1 - \delta_{N_{\text{not}\alpha}})P(-N_1, N_2)].\end{aligned} \tag{6}$$

For the symbol ± in the second term when $\alpha = 1$ I take "+" when $j =$ even and "−" when $j =$ odd, and when $\alpha = 2$ I take "+" when $i =$ odd and " −" when $i =$ even. The reciprocal relations are manifest

$$G^{(1)}_{m,m+1} = G^{(2)}_{m,m+1} \quad \text{for } m \geq 0 \tag{7}$$

and

$$G^{(1)}_{m,m} = G^{(2)}_{m-1,m+1}, \qquad G^{(1)}_{m-1,m+1} = G^{(2)}_{m,m} \quad \text{for } m > 0. \tag{8}$$

Equations (7) and (8) are exact relations that follow deductively from Eq. (2). Similar symmetry relations derived from an entirely different perspective have been given by Saito and Utsumi [18]. Equations (7) and (8) include the "linear" reciprocal relation $G^{(1)}_{0,1} = G^{(2)}_{0,1}$ that quantifies the first order effect of $\Delta\mu_2$ on $\langle N_1\rangle$ to the effect of $\Delta\mu_1$ on $\langle N_2\rangle$, and also quadratic reciprocal relations $G^{(1)}_{1,1} = G^{(2)}_{0,2}$ and $G^{(1)}_{0,2} = G^{(2)}_{1,1}$ coupling the joint (bilinear) effect of $\Delta\mu_1\Delta\mu_2$ on $\langle N_1\rangle$ to the "quadratic" effect of $\Delta\mu_1^2$ on $\langle N_2\rangle$ and vice versa. These low order terms ($m < 2$) are likely to be the terms of greatest experimental significance. Nevertheless, the reciprocal relations for higher order terms ($m \geq 2$) are also valid. The reciprocal relations Eqs. (7) and (8) quantify the symmetry of the interactions between the particles in the two channels and how this leads to interference between the two transport processes.

The conductances $G^{(\alpha)}_{i,j}$ are functions of $\Delta\mu_1$ and $\Delta\mu_2$. This makes it difficult to use these reciprocal relations for interpreting experiments since it is impossible to separate the $\Delta\mu_1$ and $\Delta\mu_2$ dependencies coming from the $G^{(\alpha)}_{i,j}$ from the dependencies arising from the exponential weighting factors in Eq. (3). However, one can expand the $G^{(\alpha)}_{i,j}$ themselves in powers of $\Delta\mu_1$ and $\Delta\mu_2$,

$$G^{(\alpha)}_{i,j} = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty} g^{(\alpha)}_{i,j;k,l}\Delta\mu_\alpha^k \Delta\mu^l_{\mathrm{not}\alpha}, \qquad \alpha = 1, 2. \tag{9}$$

The $g_{i,j;k,l}$ are constant ($\Delta\mu_1$ and $\Delta\mu_2$ independent) coefficients. From Eq. (7) $g^{(1)}_{m,m+1;k,l} = g^{(2)}_{m,m+1;k,l}$ and from Eqs. (8) $g^{(1)}_{m,m;k,l} = g^{(2)}_{m-1,m+1;k,l}$ and $g^{(1)}_{m-1,m+1;k,l} = g^{(2)}_{m,m;k,l}$ for all $k, l \geq 0$. By inserting the expansion for the $G_{i,j}$ into Eq. (5) one finds to second order

$$\begin{aligned}\langle N_{1,\mathrm{c}}\rangle &\approx L\Delta\mu_2 + (C + M)\Delta\mu_1\Delta\mu_2 + (Q + M^*)\Delta\mu_2^2,\\ \langle N_{2,\mathrm{c}}\rangle &\approx L\Delta\mu_1 + (C + M^*)\Delta\mu_1\Delta\mu_2 + (Q + M)\Delta\mu_1^2.\end{aligned} \tag{10}$$

The coefficients denoted by capital letters L (linear), C (cross), and Q (quadratic) are $\Delta\mu_1$ and $\Delta\mu_2$ independent coefficients that come from relation Eq. (7), $L = g^{(1)}_{0,1;0,0} = g^{(2)}_{0,1;0,0}$, $C = g^{(1)}_{0,1;1,0} = g^{(2)}_{0,1;1,0}$, $Q = g^{(1)}_{0,1;0,1} = g^{(2)}_{0,1;0,1}$. The new reciprocal relations [from Eq. (8)] are

$$g^{(1)}_{1,1;0,0} = g^{(2)}_{0,2;0,0} = M, \qquad g^{(2)}_{1,1;0,0} = g^{(1)}_{0,2;0,0} = M^* \tag{11}$$

where M and M^* are also $\Delta\mu_1$ and $\Delta\mu_2$ independent coefficients.

The reciprocal relations alone, of course, do not assure coupling. If both wells are symmetric all coupling coefficients will be zero. If symmetry is broken in both wells, and the wells are close enough together that coupling is experimentally measurable, Eq. (10) can be used to experimentally determine the coefficients in a straightforward way. The $\langle N_{\alpha,d}\rangle$ can be determined by measuring both $\langle N_\alpha\rangle$ with $\Delta\mu_{\mathrm{not}\alpha} = 0$, and L and $(Q + M^*)$ and $(Q + M)$ can be determined by measuring both $\langle N_\alpha\rangle$ with $\Delta\mu_\alpha = 0$. Finally, $(C + M)$ and $(C + M^*)$ can be determined by measuring both $\langle N_\alpha\rangle$ with both $\Delta\mu_{\mathrm{not}\alpha} \neq 0$ and $\Delta\mu_\alpha \neq 0$. A third intriguing possibility is that only one well has broken symmetry as shown in Fig. 3, where the well corresponding to $\mathcal{M}_1$ is drawn as an asymmetric sawtooth but the well corresponding to $\mathcal{M}_2$ has left or right reflection symmetry. Coupling of transport through $\mathcal{M}_1$ to transport through $\mathcal{M}_2$ can occur by a well-known "flashing ratchet" mechanism [19] where the increase and decrease $\delta n_2(t)$ of the particle number in $\mathcal{M}_2$ raises and lowers the energy levels in $\mathcal{M}_1$. When $\Delta\mu_2 \neq 0$ the resulting nonequilibrium fluctuation of the energy levels, in conjunction with the asymmetry of the well, leads to transport from left to right through $\mathcal{M}_1$ even when $\Delta\mu_1$ is zero or slightly negative. Such asymmetric potential wells are common, e.g., in conical nanopores that are known to rectify current [20], and for which there is evidence of coupled transport [21]. In the coupled wells in Fig. 3 $\mathcal{M}_2$ is symmetric and, hence, with $\Delta\mu_2 = 0$, $\langle N_2\rangle = 0$ irrespective of $\Delta\mu_1$, i.e., $G^{(2)}_{0,m} = 0$ for all m and, hence, $L = C = Q = M = 0$. Then, one has

$$\begin{aligned}\langle N_{1,\mathrm{c}}\rangle &\approx M^*\Delta\mu_2^2 + \mathcal{O}(3),\\ \langle N_{2,\mathrm{c}}\rangle &\approx M^*\Delta\mu_1\Delta\mu_2 + \mathcal{O}(3).\end{aligned} \tag{12}$$

A simple heuristic model illustrating nonlinear coupling that shows this pattern has been previously described [22]. The arguments here demonstrate that the reciprocity between the coefficient of the term quadratic in $\Delta\mu^2_{\mathrm{sym}}$ for

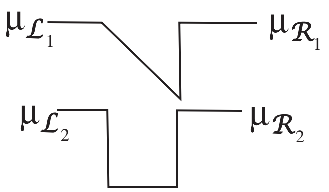

FIG. 3. If at least one of the mesoscopic regions is asymmetric one expects coupling by the Curie principle. Here the well corresponding to $\mathcal{M}_1$ is modeled as an asymmetric sawtooth, and transport from $\mathcal{L}_1$ to $\mathcal{R}_1$ will be driven by a flashing ratchet mechanism using energy released by downhill transport of particles between $\mathcal{L}_2$ and $\mathcal{R}_2$ with $\Delta\mu_2 \neq 0$.

$\langle N_{\mathrm{asym}}\rangle$ and the coefficient of the bilinear term $\Delta\mu_{\mathrm{sym}}\Delta\mu_{\mathrm{asym}}$ for $\langle N_{\mathrm{sym}}\rangle$ in the case where one well is symmetric (sym) and the other asymmetric (asym) is general.

In the Coulomb blockade regime no more than one charge can reside in each mesoscopic region at a time so the number of particles transported between the two reservoirs in one cycle of excursion away from and return to the steady state can only take on the values $N_1 = -1, 0$, or $+1$ and $N_2 = -1, 0$, or $+1$. Then the sum in Eq. (4) can be truncated at $N_1 = 1$ and $N_2 = 1$ and all coefficients can be expressed in terms of only two functions, the sum $A = P(1,1) + P(-1,1)$ and difference $B = P(1,1) - P(-1,1)$ of the coupled stepping probabilities, giving rise to the closed form expressions for the coupled transport,

$$\begin{aligned}\langle N_{1,c}\rangle &= B - e^{\Delta\mu_2}[B\cosh(\Delta\mu_1) + A\sinh(\Delta\mu_1)],\\ \langle N_{2,c}\rangle &= A - e^{\Delta\mu_2}[A\cosh(\Delta\mu_1) + B\sinh(\Delta\mu_1)],\end{aligned} \tag{13}$$

where all dependence of the transport on the structure of the mesoscopic region, and on kinetic aspects (e.g., relative heights of barriers and whether the transport occurs by ballistic or diffusive mechanisms) is contained in the two functions A and B.

The symmetry relations Eqs. (7), (8), (10), and (13) derived here pertain to a wide variety of coupled transport processes that can be described in terms of discrete events, including coupled chemical reactions, and biological transport processes such as active transport [6], coupled transport across membranes [9], and molecular motors [10–12], where the protein that mediates the transport is the fluctuating mesoscopic region. The protein can be viewed as a "conduit" for energy to flow between two macroscopic sources (e.g., the free energy difference of fuel and product, and the viscous bath and any external applied force in the case of a molecular motor), but is itself in mechanical equilibrium at every instant [12].

Onsager, in deriving the reciprocal relations [2] for which he won the Nobel prize in 1968, was limited by the experimental capabilities of his day, where it was generally only possible to measure currents and voltages or other similar quantities—thermodynamic flows and forces. Now that experiments measuring discrete processes—transfer of individual charges [15], single steps along a polymer lattice [23], and single chemical conversions between a substrate and product pair by an enzyme [24]—are routinely accomplished we can focus on the differences and ratios between the numbers of these elementary events in any time interval to see that the deep symmetry relations uncovered by Onsager well over half a century ago are applicable beyond the near to thermodynamic equilibrium regime.

I thank Charles Smith and Jim McClymer for very useful discussions, and Leo Kadanoff, Tom Witten, Kostantine Turitsyn, Stuart Rice, and John Ross for their valuable comments.

---

[*] astumian@maine.edu

[1] M. Buttiker, Phys. Rev. Lett. **57**, 1761 (1986).

[2] L. Onsager, Phys. Rev. **38**, 2265 (1931).

[3] H. B. G. Casimir, Rev. Mod. Phys. **17**, 343 (1945).

[4] D. Sanchez and K. Kang, Phys. Rev. Lett. **100**, 036806 (2008).

[5] C. Livermore, C. H. Crouch, R. M. Westervelt, K. L. Campman, and A. C. Gossard, Science **274**, 1332 (1996).

[6] P. Lauger, *Electrogenic Ion Pumps* (Sinauer, Sunderland, MA, 1991).

[7] A. Katchalsky and P. F. Curran, *Nonequilibrium Thermodynamics in Biophysics* (Harvard University Press, Cambridge, MA, 1967).

[8] T. L. Hill, *Free Energy Transduction in Biology* (Academic Press, New York, NY, 1977).

[9] R. D. Astumian, P. B. Chock, T. Y. Tsong, and H. V. Westerhoff, Phys. Rev. A **39**, 6416 (1989).

[10] F. Julicher, A. Ajdari, and J. Prost, Rev. Mod. Phys. **69**, 1269 (1997).

[11] R. D. Astumian, Science **276**, 917 (1997).

[12] R. D. Astumian, Phys. Chem. Chem. Phys. **9**, 5067 (2007).

[13] I. Derenyi and R. D. Astumian, Phys. Rev. E **58**, 7781 (1998).

[14] M. Bier, M. Kostur, I. Derenyi, and R. D. Astumian, Phys. Rev. E **61**, 7184 (2000).

[15] Y. V. Nazarov, Ann. Phys. (Leipzig) **16**, 720 (2007).

[16] T. L. Hill, Biochemistry **14**, 2127 (1975).

[17] J. Tobiska and Y. V. Nazarov, Phys. Rev. B **72**, 235328 (2005).

[18] K. Saito and Y. Utsumi, arXiv:0709.4128v1.

[19] R. D. Astumian and P. Hanggi, Phys. Today **55**, No. 11, 33 (2002).

[20] Z. S. Siwy and A. Fulinski, Phys. Rev. Lett. **89**, 198103 (2002).

[21] Z. S. Siwy, M. R. Powell, E. Kalman, R. D. Astumian, and R. S. Eisenberg, Nano Lett. **6**, 473 (2006).

[22] R. D. Astumian, Appl. Phys. A **75**, 193 (2002).

[23] K. Svoboda, C. Schmidt, B. J. Schnapp, and S. M. Block, Nature (London) **365**, 721 (1993).

[24] H. P. Lu, L. Xun, and S. Xie, Science **282**, 1877 (1998).