Comment on "Reciprocal Relations for Nonlinear Coupled Transport"

In a recent Letter, Astumian [1] described an interesting procedure which allows one to determine higher-order reciprocity relations for nonlinear coupled transport based on the fluctuation relation alone. In this Comment, I would like to show that the symmetry relations used by Astumian can provide information on reciprocity of linear coefficients only (i.e., one can rederive Onsager's relations), consistent with the fact that the sole basis for the relations is the microscopic reversibility used originally by Onsager. The higher-order coefficients derived in the Letter are, in fact, incomplete and do not provide additional constraints on the magnitude of coefficients.

In the Letter [1], the expression for the number of particles transferred during the excursion away from equilibrium is separated into two parts: $\langle N_\alpha\rangle = \langle N_{\alpha,d}\rangle + \langle N_{\alpha,c}\rangle$, where $N_{\alpha,d}$ represents direct terms that vanish when direct force vanishes (i.e., $\langle N_{\alpha,d} = 0\rangle$ when $\Delta\mu_\alpha = 0$), and $\langle N_{\alpha,c}\rangle$ represents the remaining terms which contain cross dependence on $\Delta\mu_{\mathrm{not}\alpha}$. In deriving the formulas for reciprocity relations, Astumian incorrectly assumes that $\langle N_{\alpha,d}\rangle$ does not depend on $\Delta\mu_{\mathrm{not}\alpha}$. In this Comment, I point out that $\langle N_{\alpha,d}\rangle$, as defined in [1], generally depends on both $\Delta\mu_1$ and $\Delta\mu_2$ by providing a simple example. Establishing this dependence, I proceed to modify the derivation given in [1] and provide corrected general expression for higher-order terms.

As an example, I consider two transport processes coupled as follows. First system consists of left $\mathcal{L}_1$ and right $\mathcal{R}_1$ reservoirs which are connected to the opposite sides of a mesoscopic region $\mathcal{M}_1$ (see Fig. 1 of [1]). Particles can reversibly move between the reservoirs and the mesoscopic region in accord with the following kinetic parameters: $k_{-\mathcal{L}_1}$ is the rate with which particles move from $\mathcal{L}_1$ to $\mathcal{M}_1$, and $k_{\mathcal{L}_1}$ is the rate of reverse process. Similarly, $k_{\mathcal{R}_1}$ defines the rate with which the particles jump from $\mathcal{M}_1$ to $\mathcal{R}_1$ with the $k_{-\mathcal{R}_1}$ being the rate of the reverse process. Second system possesses similar structure with $\mathcal{L}_2$, $\mathcal{M}_2$, and $\mathcal{R}_2$. At this point, we introduce the restriction that at any moment of time, there can only be one particle in both $\mathcal{M}_1$ and $\mathcal{M}_2$ (i.e., there can never simultaneously be one particle in $\mathcal{M}_1$ and one particle in $\mathcal{M}_2$). Coupling between the fluxes J_1 and J_2 arises as a consequence of this restriction.

Now, the property of interest is the number of particles transferred between reservoirs during the single excursion away from steady state. Starting point of derivation in Ref. [1] is symmetry relation following from microscopic reversibility that connects $P(N_1, N_2)$ and $P(-N_1, -N_2)$. For this system, it is easy to determine N_1 and N_2, numbers of particles transferred between the reservoirs of each system during the excursion away from steady state. Indeed, possible values that N_α can take are $-1, 0, +1$. To see this, start with 0 particles in mesoscopic region $\mathcal{M}$; we will leave this state when a particle enters $\mathcal{M}$ from any of the reservoirs, but immediately return to this state after particle jumps out of $\mathcal{M}$. We see that there are five nonzero excursion probabilities $P(+1, 0)$, $P(-1, 0)$, $P(0, 0)$, $P(0, +1)$, $P(0, -1)$ and they can be easily computed as: $P(+1, 0) \propto k_{-\mathcal{L}_1}k_{\mathcal{R}_1}$, $P(-1, 0) \propto k_{-\mathcal{R}_1}k_{\mathcal{L}_1}$, $P(0, +1) \propto k_{-\mathcal{L}_2}k_{\mathcal{R}_2}$, $P(0, -1) \propto k_{-\mathcal{R}_2}k_{\mathcal{L}_2}$, $P(0, 0) \propto (k_{-\mathcal{L}_1}k_{\mathcal{L}_1} + k_{-\mathcal{L}_2}k_{\mathcal{L}_2} + k_{-\mathcal{R}_1}k_{\mathcal{R}_1} + k_{-\mathcal{R}_2}k_{\mathcal{R}_2})$, where proportionality constant $\mathcal{C}$ ensures that some of all these probabilities is equal to 1. We notice an important feature that dependence on the $\Delta\mu_2$ in expression for probability $P(N_1, 0)$ comes through the proportionality factor and, therefore, does not contribute to the symmetry relation (Eqn. (2) in [1]).

In the coupled systems, such as this one, each flux depends on both driving forces. For example, expression for the average number of particles transported during the excursion away from equilibrium $N_1(\Delta\mu_1, \Delta\mu_2)$ can be written for this system as

$$\langle N_1\rangle = \sum_{N_1,N_2} N_1 P(N_1, N_2) = P(+1, 0)(1 - e^{-N_1\Delta\mu_1}) \quad (1)$$

with the understanding that dependence on $\Delta\mu_2$ comes through $P(+1, 0)$. We see that "coupled" term, as defined by [1], is zero for this system $\langle N_{1,c}\rangle = 0$ and, hence, $\langle N_{1,d}\rangle = \langle N_1\rangle$.

Having established that $\langle N_{1,d}\rangle$ generally depends on both the $\Delta\mu_1$ and $\Delta\mu_2$, we can proceed to derive higher-order coefficients following the recipe suggested by [1]. The only modification is that we need to take care of the $G_i^{(\alpha)}$ depending on both $\Delta\mu$'s. The expansion of the "direct" term introduces additional terms into higher-order coupled coefficient, here denoted as X and Y, that are not restricted by any relations. So, to the second order, we have

$$\begin{aligned}\langle N_1\rangle &\approx f_1(\Delta\mu_1) + L\Delta\mu_2 + (X + C + M)\Delta\mu_1\Delta\mu_2 \\ &\quad + (Q + M^*)\Delta\mu_2^2, \\ \langle N_2\rangle &\approx f_2(\Delta\mu_2) + L\Delta\mu_1 + (Y + C + M^*)\Delta\mu_1\Delta\mu_2 \\ &\quad + (Q + M)\Delta\mu_1^2.\end{aligned} \quad (2)$$

If one were to measure experimentally second order coefficients, the relations (3) could not provide additional restrictions on the magnitudes of coefficients even in the specially symmetric cases.

Maxim N. Artyomov
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139, USA

Received 15 January 2009; published 8 April 2009
DOI: 10.1103/PhysRevLett.102.149701
PACS numbers: 73.23.−b, 73.50.Fq

[1] R. D. Astumian, Phys. Rev. Lett. **101**, 046802 (2008).

