Astumian Replies: In the preceding Comment [1], Maxim Artyomov suggests that the coefficients for higher-order reciprocal relations I derived in [2] are incomplete. This claim is based on his correct observation that in my separation of terms into a "direct" term (d) and a "cross" term (c), $\langle N_\alpha \rangle = \langle N_{\alpha,d} \rangle + \langle N_{\alpha,c} \rangle$; the direct terms do in fact depend on the magnitude of both driving terms $\Delta\mu_1$ and $\Delta\mu_2$, in contradiction to my statement that $\langle N_{\alpha,d} \rangle$ depends only on $\Delta\mu_\alpha$. The experimental relevance of this separation is that $\langle N_{\alpha,d} \rangle = 0$ when $\Delta\mu_\alpha = 0$. The independence on $\Delta\mu_{\mathrm{not}\alpha}$ was not "assumed," however, since my incorrect assertion was not used in the subsequent derivation. Artyomov further asserts that the higher-order relations provide no additional experimental constraints on the system, a claim with which I disagree.

To see why the generalized symmetry relations [2] are in fact experimentally important, let us follow a recent and more general derivation [3]. Starting with a relation derived from microscopic reversibility,

$$\frac{P(N_1, N_2)}{P(-N_1, -N_2)} = e^{N_1 \Delta\mu_1 + N_2 \Delta\mu_2}, \tag{1}$$

and working in units such that the product of Boltzmann's constant and the Kelvin temperature is unity, $k_B T = 1$, we write the statistical moments for the numbers of charges transported during each excursion away from and return to the steady state as

$$\langle N_1^n N_2^m \rangle = \sum_{N_1, N_2 = -\infty}^{+\infty} N_1^n N_2^m P(N_1, N_2). \tag{2}$$

Using Eq. (1) in Eq. (2) and expanding in powers of $\Delta\mu_1$ and $\Delta\mu_2$, we derive [3]

$$\langle N_1^n N_2^m \rangle = \sum_{p=0}^{\infty} \sum_{q=0}^{p} [2D_{q,p-q}^{(n,m)} + L_{q,p-q}^{(n,m)}] \frac{\Delta\mu_1^q \Delta\mu_2^{p-q}}{q!(p-q)!} \tag{3}$$

where $L_{0,0}^{(n,m)} = 0$, and $D_{q,p-q}^{(n,m)} = 0$ for $n + m = \mathrm{odd}$. The coefficients obey the general reciprocal relations

$$L_{1,0}^{(n,m)} = L_{0,1}^{(n+1,m-1)}, \qquad n \geq 0, \qquad m \geq 1 \tag{4}$$

and the general fluctuation-dissipation (GFD) relations

$$\begin{aligned} L_{a,0}^{(n,m)} &= L_{a-1,0}^{(n+1,m)} + D_{a-1,0}^{(n+1,m)}, \\ L_{0,b}^{(n,m)} &= L_{0,b-1}^{(n,m+1)} + D_{0,b-1}^{(n,m+1)}, \\ L_{a,b}^{(n,m)} &= L_{a,b-1}^{(n,m+1)} + D_{a,b-1}^{(n,m+1)} + D_{a-1,b}^{(n+1,m)} \\ &\text{for } n+m = \mathrm{odd}; \qquad a, b > 0. \end{aligned} \tag{5}$$

All coefficients are independent of $\Delta\mu_1$ and $\Delta\mu_2$ and are dimensionless since we focused not on currents but on the number of charges transported during one cycle of fluctuation of the mesoscopic system away from and return to a steady-state occupancy. Unlike the Stokes-Einstein fluctuation-dissipation relation and the Onsager reciprocal relation for the coefficients in expressions for currents (i.e., for number of charges transported per unit time), the relations in Eqs. (4) and (5) are exact. By using these relations, the equations for the averages $\langle N_\alpha \rangle$ through second order can be cast in the form

$$\begin{aligned} \langle N_1 \rangle &= f_1 + L\Delta\mu_2 + (M + C)\Delta\mu_1\Delta\mu_2 + M^*\Delta\mu_2^2 + \cdots \\ \langle N_2 \rangle &= f_2 + L\Delta\mu_1 + (M^* + C^*)\Delta\mu_1\Delta\mu_2 + M\Delta\mu_1^2 + \cdots \end{aligned} \tag{6}$$

where f_α are functions of $\Delta\mu_\alpha$ only, and where $L = L_{0,1}^{(1,0)} = L_{1,0}^{(0,1)}$; $M = L_{2,0}^{(0,1)}$; $M^* = L_{0,2}^{(1,0)}$; $C = D_{1,0}^{(0,2)}$; and $C^* = D_{0,1}^{(2,0)}$. The linear relations are particularly experimentally useful since the reciprocal relation reduces the number of coefficients to first order for the averages from four to three, and the fluctuation-dissipation relations allow these three coefficients to be determined by measuring the cumulants with both $\Delta\mu_\alpha = 0$. The second order relations are also very important experimentally—for some devices (i.e., if either well is symmetric), the linear coupling coefficient L is identically zero by symmetry [4], and the lowest order coupling possible is at second order. If well 1 is symmetric, then $\langle N_1 \rangle = 0$ if $\Delta\mu_1 = 0$ and hence $L_{0,p}^{(n,0)} = D_{0,p}^{(n,0)} = 0$ and thus $M^* = C^* = 0$. If well 2 is symmetric, then $\langle N_2 \rangle = 0$ if $\Delta\mu_2 = 0$ and hence $L_{q,0}^{(0,m)} = D_{q,0}^{(0,m)} = 0$ and thus $M = C = 0$. Once it is established that $L = 0$, if, e.g., $M \neq 0$, we can immediately conclude that $M^* = C^* = 0$, and so Artyomov is incorrect in the assertion that the nonlinear relations do not provide new experimental constraints, especially when used in conjunction with spatial symmetry considerations. I certainly agree that further research is important to see whether additional constraints can be derived, e.g., for systems where "slip" is effectively excluded, i.e., where $P(N_1, 0) = P(0, N_2) \approx 0$, since approaching this limit is a significant goal for design of coupled devices.

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[1] M. Artyomov, preceding Comment, Phys. Rev. Lett. **102**, 149701 (2009).
[2] R. D. Astumian, Phys. Rev. Lett. **101**, 046802 (2008).
[3] R. D. Astumian, Phys. Rev. E **79**, 021119 (2009).
[4] M. Bier, M. Kostur, I. Derenyi, and R. D. Astumian, Phys. Rev. E **61**, 7184 (2000).

