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Reciprocity conditions for a quasilinear uniform barrier

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We consider the steady flow of K interacting currents through a uniform barrier composed of material satisfying a linear flow equation $J_m = \gamma_{mn}(\beta)(d\beta_n/dx)$. β_k is the affinity associated with the current J_k. Using nonlinear reciprocity relations previously derived from microscopic time reversibility we derive a set of nonlinear constraints involving the derivatives of the conductivity matrix γ_{ij} with respect to the affinities $\beta_1, \ldots, \beta_K$. The constraints are verified with the use of a model of ideal-gas flow through a porous plug.

I. INTRODUCTION

We shall consider the steady, one-dimensional flow of K conserved quantities (e.g., energy and electric charge) through a barrier composed of uniform material. We shall assume that the local current of the ith conserved quantity $J_i(x)$ is exactly proportional to the gradients of the affinities of all K quantities

$$J_i = \gamma_{ij}(\beta)\beta_j'(x) . \tag{1}$$

[In Eq. (1) summation over j is understood.] For a system satisfying time-reversible dynamics the linear conductivity matrix γ_{ij}, which usually depends on the local values of the affinities $\beta = (\beta_1, \ldots, \beta_K)$, can be shown to be symmetric.[1,2]

For a material that satisfies a linear flow equation [i.e., Eq. (1)] it might be supposed that the Onsager reciprocity relation $\gamma_{ij} = \gamma_{ji}$, exhausts the consequences of the time reversibility of the underlying dynamics. We shall show that this is not so and that one can derive conditions on the derivatives, with respect to the β_n of the elements of $\gamma_{ij}(\beta)$. Some of these conditions will involve derivatives of the diagonal elements, about which the linear Onsager relation says nothing.

In standard mathematical terminology, Eq. (1) is a system of quasilinear equations, not a system of linear equations. Because of the dependence of γ_{ij} on β the sum of two solutions is in general not a solution. This nonlinearity manifests itself in a nonlinear relationship between the currents through the barrier and the imposed affinity differences across the faces of the barrier. Let us define the constants σ_i and $\bar{\beta}_i$ by

$$\beta_i^R - \beta_i^L = 2\sigma_i \tag{2}$$

and

$$\beta_i^R + \beta_i^L = 2\bar{\beta}_i , \tag{3}$$

where β_i^L and β_i^R are the imposed affinities on the left and right faces of the barrier. We define K functions $y_i(x)$ as deviations of $\beta_i(x)$ from $\bar{\beta}_i$:

$$y_i(x) = \beta_i(x) - \bar{\beta}_i . \tag{4}$$

As a result of the uniformity of the barrier composition the steady-state currents through the barrier are odd functions of the σ_i's; that is,

$$J_i(\bar{\beta}_i, \ldots, \bar{\beta}_K, -\sigma_1, \ldots, -\sigma_K) = -J_i(\bar{\beta}_1, \ldots, \bar{\beta}_K, \sigma_1, \ldots, \sigma_K) . \tag{5}$$

From now on we shall suppress the writing of the average affinities. We assume that J_i can be expanded in a power series in the affinity differences. We shall keep only the first nonlinear term. The generalization to an arbitrary number of terms is obvious but tedious:

$$J_i = A_{ij}\sigma_j + B_{ijkl}\sigma_j\sigma_k\sigma_l . \tag{6}$$

We shall also expand the conductivity matrix $\gamma_{ij}(\beta)$ about the value $\bar{\beta}$:

$$\gamma_{ij} = P_{ij} + Q_{ij}^k y_k + R_{ij}^{kl} y_k y_l + \cdots . \tag{7}$$

When the nonlinear term in Eq. (6) can be neglected the Onsager reciprocity theorem shows that A_{ij} is a symmetric matrix. In a previous paper[3] it was shown that B_{ijkl} is also a completely symmetric tensor. By solving the differential equations [Eq. (1)] by a perturbation method we shall express B in terms of P, Q, and R. The symmetry requirements on B will then impose restrictions on the Q and R coefficients. We imbed Eq. (1) in a family of equations dependent on a parameter ϵ with $0 \le \epsilon \le 1$. We let

$$\gamma_{ij} = P_{ij} + \epsilon Q_{ij}^k y_k + \epsilon^2 R_{ij}^{kl} y_k y_l + \cdots \tag{8}$$

and look for a solution of the form

$$y_n(x)=f_n(x)+\epsilon g_n(x)+\epsilon^2 h_n(x)+\cdots \qquad (9)$$

with

$$J_i=J_i^0+\epsilon J_i^1+\epsilon^2 J_i^2+\cdots \ . \qquad (10)$$

For simplicity we shall assume that the barrier material extends from $x=-1$ to 1. In order for the boundary conditions to be satisfied at all values of ϵ we must have

$$f_n(\pm 1)=\pm\sigma_n \qquad (11)$$

and

$$g_n(\pm 1)=h_n(\pm 1)=\cdots=0 \ . \qquad (12)$$

Putting these assumed forms into Eq. (1) we obtain

$$\sum_n \epsilon^n J_i^n-[P_{ij}+\epsilon Q_{ij}^k(f_k+\epsilon g_k+\cdots)+\epsilon^2 R_{ij}^{kl}(f_k+\cdots)(f_l+\cdots)](f_j'+\epsilon g_j'+\epsilon^2 h_j'+\cdots)=0 \ . \qquad (13)$$

Setting to zero the coefficients of separate powers of ϵ and using the boundary conditions on f_i, g_i, and h_i we obtain equations that allow the determination of J_i^0, J_i^1, J_i^2, etc.

The zero-order term gives

$$J_i^0-P_{ij}f_j'=0 \ , \qquad (14)$$

which implies that $f_j'(x)=\text{const}$. The boundary condition then gives

$$f_j(x)=\sigma_j x \qquad (15)$$

and

$$J_i^0=P_{ij}\sigma_j \ . \qquad (16)$$

The first-order term is

$$J_i^1-P_{ij}g_j'-Q_{ij}^k f_k f_j'=0 \ , \qquad (17)$$

which yields

$$g_j'(x)=P_{jk}^{-1}J_k^1-xP_{jl}^{-1}Q_{lm}^k\sigma_k\sigma_m \qquad (18)$$

and finally

$$g_j(x)=C+xP_{jk}^{-1}J_k^1-\tfrac{1}{2}x^2P_{jl}^{-1}Q_{lm}^k\sigma_k\sigma_m \ . \qquad (19)$$

Using the boundary conditions one gets

$$g_j(x)=\tfrac{1}{2}(1-x^2)P_{jl}^{-1}Q_{lm}^k\sigma_k\sigma_m \qquad (20)$$

and

$$J_k^1=0 \ . \qquad (21)$$

In a similar way the next term gives

$$J_i^2=\tfrac{1}{3}[R_{ia}^{bc}+(Q_{ia}^k-Q_{ik}^a)P_{kl}^{-1}Q_{lb}^c]\sigma_a\sigma_b\sigma_c \ . \qquad (22)$$

II. CONSEQUENCES OF RECIPROCITY

That B_{ijkl} is a completely symmetric tensor implies that

$$\frac{\partial J_i^2}{\partial\sigma_j}-\frac{\partial J_j^2}{\partial\sigma_i}=0 \ . \qquad (23)$$

Using Eq. (22) in Eq. (23) gives our basic constraint on the expansion coefficients of γ_{ij}:

$$[2(R_{im}^{jn}-R_{jm}^{in})-(Q_{ik}^j-Q_{jk}^i)P_{kl}^{-1}Q_{lm}^n+(Q_{im}^kQ_{jl}^n-Q_{jm}^kQ_{il}^n)P_{kl}^{-1}+(Q_{im}^kQ_{ln}^j-Q_{jm}^kQ_{ln}^i)P_{kl}^{-1}$$
$$+(Q_{ln}^iQ_{jk}^m-Q_{ln}^jQ_{ik}^m)P_{kl}^{-1}]\sigma_m\sigma_n=0 \ , \qquad (24)$$

which should be valid for arbitrary values of $\sigma_1,\ldots,\sigma_K$ and all $i\neq j$.

Introducing the notational device

$$[F_{ija}]_{ij}^{\pm}=F_{ija}\pm F_{jia} \qquad (25)$$

we can write Eq. (24) in the form

$$[[2R_{im}^{jn}+(Q_{jk}^iQ_{lm}^n+Q_{im}^kQ_{jl}^n+Q_{im}^kQ_{ln}^j$$
$$+Q_{km}^iQ_{jl}^n)P_{kl}^{-1}]_{mn}^{+}]_{ij}^{-}=0 \ . \qquad (26)$$

For a system involving two interacting currents, Eq. (26) gives three independent linear relations, one for each of the combinations $(i,j,m,n)=(1,2,1,1)$, $(1,2,1,2)$, and $(1,2,2,2)$.

III. GAS FLOW THROUGH A POROUS PLUG

As a system on which to test the predictions of Eq. (26) we shall use the following model of ideal-gas flow through a porous plug. We model the

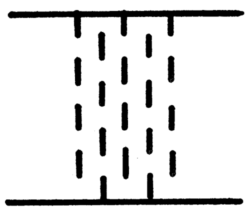

FIG. 1. A model of a porous plug.

porous plug by a sequence of closely spaced perforated baffles (Fig. 1). For each baffle the sum of the areas of all the holes is A. The two conserved quantities whose flow we study are particle number and energy. The associated affinities are $\beta_1 = \partial S/\partial N = -\mu/kT$ and $\beta_2 = \partial S/\partial E = 1/kT$. Assuming that the affinity differences $\Delta\beta_1$ and $\Delta\beta_2$ across any one baffle are very small a straightforward calculation shows that the rate of flow of particles and energy through the baffle are given, respectively, by

$$J_1 = \lambda e^{-\beta_1} \left[\frac{\Delta\beta_1}{\beta_2^2} + 2\frac{\Delta\beta_2}{\beta_2^3} \right] \tag{27}$$

and

$$J_2 = 2\lambda e^{-\beta_1} \left[\frac{\Delta\beta_1}{\beta_2^3} + 3\frac{\Delta\beta_2}{\beta_2^4} \right] , \tag{28}$$

where $\lambda = 9A/4e^{5/2}\sqrt{3\pi m}$. Thus the elements of the conductivity matrix are $\gamma_{11} = \lambda\beta_2^{-2}e^{-\beta_1}$, $\gamma_{12} = \gamma_{21} = 2\lambda\beta_2^{-3}e^{-\beta_1}$, and $\gamma_{22} = 6\lambda\beta_2^{-4}e^{-\beta_1}$. From this we can obtain the arrays P, Q, and R defined in Eq. (7):

$$P_{mn} = \lambda\beta_2^{-3}e^{-\beta_1} \begin{bmatrix} \beta_2 & 2 \\ 2 & 6/\beta_2 \end{bmatrix} = -Q^1_{mn} , \tag{29}$$

$$Q^2_{mn} = 2\lambda\beta_2^{-4}e^{-\beta_1} \begin{bmatrix} \beta_2 & 3 \\ 3 & 12/\beta_2 \end{bmatrix} . \tag{30}$$

The needed elements of R are

$$R^{11}_{12} = R^{12}_{11} = \lambda\beta_2^{-3}e^{-\beta_1} , \tag{31}$$

$$R^{11}_{22} = R^{22}_{12} = 3\lambda\beta_2^{-4}e^{-\beta_1} , \tag{32}$$

and

$$R^{12}_{22} = R^{22}_{12} = 12\lambda\beta_2^{-4}e^{-\beta_1} . \tag{33}$$

The 2×2 matrix P can be inverted, giving

$$P^{-1}_{mn} = \lambda^{-1}\beta_2^3 e^{\beta_1} \begin{bmatrix} 3/\beta_2 & -1 \\ -1 & \beta_2/2 \end{bmatrix} . \tag{34}$$

Equation (26) yields the three independent relations

$$R^{12}_{11} - R^{11}_{12} + (Q^1_{2k}Q^1_{1l} + \tfrac{1}{2}Q^k_{11}Q^1_{2l} + \tfrac{1}{2}Q^k_{11}Q^2_{1l} - Q^2_{1k}Q^1_{1l} - Q^k_{12}Q^1_{1l})P^{-1}_{kl} = 0 , \tag{35}$$

$$R^{22}_{11} - R^{11}_{22} + (Q^k_{11}Q^2_{2l} + Q^1_{2k}Q^1_{2l} - Q^2_{1k}Q^2_{1l} - Q^k_{22}Q^1_{1l})P^{-1}_{kl} = 0 , \tag{36}$$

and

$$R^{22}_{12} - R^{12}_{22} + (Q^1_{2k}Q^2_{2l} + Q^k_{12}Q^2_{2l} - Q^2_{1k}Q^2_{2l} - \tfrac{1}{2}Q^k_{22}Q^2_{1l} - \tfrac{1}{2}Q^k_{22}Q^1_{2l})P^{-1}_{kl} = 0 . \tag{37}$$

A short calculation confirms that these three relations are satisfied by the arrays P, Q, and R given above.

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