

# Symmetry Properties of Nonlinear Barrier Coefficients

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Received February 23, 1982

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This paper concerns the properties of a symmetric barrier between two reservoirs. The barrier can pass  $K$  conserved quantities. The current of the  $i$ th quantity is assumed to satisfy the nonlinear relation

$$J_i = A_{ij}\Delta\beta_j + B_{ijkl}\Delta\beta_j\Delta\beta_k\Delta\beta_l$$

where the  $\Delta\beta_i$ 's are the affinity differences across the barrier and  $A_{ij}$  and  $B_{ijkl}$  are functions of the average affinities of the reservoirs. It is shown that  $B_{ijkl}$  is symmetric in all indices.

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**KEY WORDS:** Onsager relations; reciprocity theorem; nonlinear flow.

## 1. BASIC DEFINITIONS

In this paper we shall consider a system composed of a symmetric barrier (such as a *pnp* sandwich) flanked by two large identical reservoirs. We assume that the barrier can pass  $K$  conserved quantities,  $A_1, \dots, A_K$ , which we denote collectively as  $\mathbf{A}$ . Typically  $A_1$  is internal energy while  $A_2, \dots, A_K$  are the number of  $K-1$  separately conserved particle types. By making the reservoirs large enough we can neglect the amount of  $\mathbf{A}$  contained in the barrier. We assume that the system is isolated and contains a total amount of  $\mathbf{A}$  given by  $\mathbf{A} = 2\mathbf{A}^0$ . At equilibrium  $\mathbf{A}^R = \mathbf{A}^L = \mathbf{A}^0$ , where  $\mathbf{A}^R$  and  $\mathbf{A}^L$  are the amounts of  $\mathbf{A}$  in the right and left reservoirs, respectively. As thermodynamic parameters, for defining the state of the system we shall use the  $2K$  variables  $\mathbf{A}^0 = \frac{1}{2}(\mathbf{A}^R + \mathbf{A}^L)$  and  $\boldsymbol{\alpha} = \frac{1}{2}(\mathbf{A}^R - \mathbf{A}^L)$ . Clearly  $\mathbf{A}^R = \mathbf{A}^0 + \boldsymbol{\alpha}$ ,  $\mathbf{A}^L = \mathbf{A}^0 - \boldsymbol{\alpha}$ , and  $d\boldsymbol{\alpha}/dt$  gives the rate of flow through the barrier of the  $K$  conserved quantities. The total entropy of the

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system is given by

$$S(\mathbf{A}^0, \boldsymbol{\alpha}) = F(\mathbf{A}^0 + \boldsymbol{\alpha}) + F(\mathbf{A}^0 - \boldsymbol{\alpha}) \quad (1)$$

where  $F(\mathbf{A})$  is the entropy function of one reservoir.

The  $K$  affinities,

$$\beta_i(\mathbf{A}) = \frac{\partial F(\mathbf{A})}{\partial A_i}$$

are thermodynamically conjugate to the extensive variable  $A_i$ .

We shall assume that  $F(\mathbf{A})$  is analytic at  $\mathbf{A}^0$ . Using the summation convention and the notation  $F_{ij}^0 = [\partial^2 F(A)/\partial A_i \partial A_j]_{A^0}$ , etc., we can write the affinity differences and average affinities across the barrier as expansions in  $\boldsymbol{\alpha}$ :

$$\begin{aligned} \Delta\beta_i(\mathbf{A}^0, \boldsymbol{\alpha}) &\equiv \beta_i(\mathbf{A}^0 + \boldsymbol{\alpha}) - \beta_i(\mathbf{A}^0 - \boldsymbol{\alpha}) \\ &= 2F_{ij}^0\alpha_j + \dots \end{aligned} \quad (2)$$

$$\begin{aligned} \bar{\beta}_i(\mathbf{A}^0, \boldsymbol{\alpha}) &\equiv \frac{1}{2} \beta_i(\mathbf{A}^0 + \boldsymbol{\alpha}) + \frac{1}{2} \beta_i(\mathbf{A}^0 - \boldsymbol{\alpha}) \\ &= F_i^0 + \frac{1}{2} F_{ijk}^0 \alpha_j \alpha_k + \dots \end{aligned} \quad (3)$$

In Eq. (2) and (3) we have included terms through second order in  $\boldsymbol{\alpha}$ . A quadratic reservoir is one for which  $F_{ij}^0 = 0$ . For a quadratic reservoir, constant  $\mathbf{A}^0$  implies constant  $\bar{\boldsymbol{\beta}}$  through third order in  $\boldsymbol{\alpha}$ . For such a reservoir

$$S(\mathbf{A}^0, \boldsymbol{\alpha}) = 2F^0 + F_{ij}^0\alpha_i\alpha_j \quad (4)$$

The reservoirs will be assumed to have internal conductivities for all the quantities  $A_j$  which are much larger than the corresponding conductivities of the barrier. They can then be assumed to be internally at equilibrium. The temporary state of the system is thus completely characterized by the values of  $\mathbf{A}^0$  and  $\boldsymbol{\alpha}$ . We also assume that the set of thermodynamic parameters,  $\bar{\boldsymbol{\beta}}$  and  $\Delta\boldsymbol{\beta}$ , is sufficient in the sense that the left-to-right current through the barrier is determined by their instantaneous value:

$$\frac{d\alpha_i}{dt} = J_i(\bar{\boldsymbol{\beta}}, \Delta\boldsymbol{\beta}) \quad (5)$$

Although the relationship between the sets of variables  $(\mathbf{A}^0, \boldsymbol{\alpha})$  and  $(\bar{\boldsymbol{\beta}}, \Delta\boldsymbol{\beta})$  is determined by the entropy function of the reservoirs, we shall assume that the function  $J_i(\bar{\boldsymbol{\beta}}, \Delta\boldsymbol{\beta})$  is a property of the barrier structure alone and would be unchanged if the two reservoirs were replaced by another pair of matched reservoirs.

The barrier coefficients are defined by expanding  $J_i$  as a power series in the affinity differences. We include only the first nonlinear term. The

extension of the analysis to include further terms is straightforward, however, series expansions are usually useful only if succeeding terms are of decreasing significance. Since third-order coefficients would already be difficult to measure the advantages of including further terms in the analysis are probably not worth the added complication. Thus, using the summation convention, we assume that  $J_i$  is given by

$$J_i = A_{ij}(\bar{\beta})\Delta\beta_j + B_{ijkl}(\bar{\beta})\Delta\beta_j\Delta\beta_k\Delta\beta_l \quad (6)$$

That  $J_i$  is an odd function of  $\Delta\beta$  follows from the reflection symmetry of the system. We shall show that both  $A_{ij}$  and  $B_{ijkl}$  are completely symmetric in their indices.

## 2. MICROSCOPIC ANALYSIS

We shall assume that the system satisfies classical Hamiltonian dynamics. (A quantum version of the following analysis has been constructed and leads to the same conclusions.) The state of the system is represented by a point  $z$  in a  $2N$ -dimensional phase space,  $\Gamma$ , in which we use coordinates  $(z_1, \dots, z_{2N}) = (q_1, \dots, q_N, p_1, \dots, p_N) = (q, p)$ . Within  $\Gamma$  we define two point transformations: (1) the time evolution operator  $T_t z_0 = z(t, z_0)$ , where  $z(t, z_0)$  is the solution of Hamilton's equations with initial value  $z_0$ , and (2) the time reversal operator  $Rz = (q, -p)$ . A function  $f(z)$  is called *time reversible* if  $f(Rz) = f(z)$  and time invariant if  $f(T_t z) = f(z)$  for all  $t$ . The Hamiltonian is assumed to have both properties. This implies that  $T_t R T_t z = Rz$  or, equivalently that

$$R T_t = T_{-t} R \quad (7)$$

We consider a microcanonical ensemble with density  $\rho(z) = \delta(H(z) - E)$  and note that  $\rho$  is both time invariant and time reversible. We also consider  $K$  observables  $a_1(z), \dots, a_K(z)$  which we collectively denote as  $\mathbf{a}(z)$ . For any  $t$  the  $K$  by  $K$  correlation matrix  $\mathbf{C}(t)$  is defined as

$$\mathbf{C} = \int_{\Gamma} \mathbf{a}(z) \mathbf{a}(T_t z) \rho(z) d^{2N}z \quad (8)$$

Introducing into Eq. (8) the transformation of variables  $z' = R T_t z$  and using the facts that  $\rho(z') = \rho(z)$ ,  $d^{2N}z' = d^{2N}z$ , and  $R T_t = T_{-t} R$  we write  $\mathbf{C}(t)$  as

$$\mathbf{C} = \int_{\Gamma} \mathbf{a}(R T_t z') \mathbf{a}(R z') \rho(z') d^{2N}z' \quad (9)$$

We shall now assume that each of the observables is even under time reversal:

$$a_i(Rz) = a_i(z) \quad (10)$$

Using Eq. (10) in Eq. (9) gives the result

$$C_{ij}(t) = C_{ji}(t) \quad (11)$$

The ensemble expectation values of the observables  $\mathbf{a}(z)$  yield  $K$  thermodynamic parameters which we interpret as a point  $\alpha$  in a  $K$ -dimensional parameter space  $\gamma$ :

$$\alpha = \int_{\Gamma} \mathbf{a}(z) \rho(z) d^{2N}z \quad (12)$$

In  $\gamma$  we define an ensemble entropy function  $S(\alpha)$  and a time evolution operator  $T_t$  by the equations

$$e^{S(\alpha)} = \int_{\Gamma} \delta(\mathbf{a}(z) - \alpha) \rho(z) d^{2N}z \quad (13)$$

and

$$T_t \alpha = \int_{\Gamma} \mathbf{a}(T_t z) \delta(\mathbf{a}(z) - \alpha) \rho(z) d^{2N}z / e^{S(\alpha)} \quad (14)$$

where  $\delta(\alpha)$  is a  $K$ -dimensional Dirac delta function. Without loss of generality we may assume that the maximum of  $S(\alpha)$  (i.e., the equilibrium state) occurs at  $\alpha = 0$ . With these definitions we obtain the identity

$$\begin{aligned} \mathbf{C} &= \int_{\Gamma} \mathbf{a}(z) \mathbf{a}(T_t z) \rho(z) d^{2N}z = \int_{\gamma} \int_{\Gamma} \mathbf{a}(z) \mathbf{a}(T_t z) \rho(z) \delta(\mathbf{a}(z) - \alpha) d^{2N}z d^K\alpha \\ &= \int_{\gamma} \alpha \int_{\Gamma} \mathbf{a}(T_t z) \delta(\mathbf{a}(z) - \alpha) \rho(z) d^{2N}z d^K\alpha \\ &= \int_{\gamma} \alpha T_t \alpha e^{S(\alpha)} d^K\alpha \end{aligned} \quad (15)$$

Equations (11) and (15), when combined, give the result

$$\int_{\gamma} [\alpha(T_t \alpha) - (T_t \alpha)\alpha] e^{S(\alpha)} d^K\alpha = 0 \quad (16)$$

It should be noted that the only assumptions made in deriving Eq. (16) were that  $H(z)$  and  $\mathbf{a}(z)$  are time reversible.

We define  $K$  affinities, conjugate to the  $\alpha_i$  by

$$\Delta\beta_i \equiv \frac{\partial S(\alpha)}{\partial \alpha_i} \quad (17)$$

(They are called  $\Delta\beta_i$  in order to facilitate comparison with the definitions of Section 1.) That  $T_t \alpha$  is a function of  $\alpha$  is clear from Eq. (14). We shall now assume, for  $t$  much larger than a microscopic collision time but much less than the macroscopic relaxation time of the system, that  $T_t \alpha - \alpha$  is proportional to  $t$ :

$$(T_t \alpha - \alpha) = t \mathbf{J}(\alpha) \quad (18)$$

Combining Eqs. (16) and (18) we get

$$\int_{\gamma} [\alpha_r J_j - \alpha_j J_i] e^{S(\alpha)} d^K \alpha = 0 \quad (19)$$

We now want to apply this result to the system discussed in Section 1. This requires that we reintroduce the  $K - 1$  variables  $A_2^0, \dots, A_K^0$ . ( $2A_1^0$  is the energy  $E$  used in the construction of the microcanonical ensemble.) The integral in Eq. (19) should be taken at constant  $\mathbf{A}^0$ . (The microcanonical ensemble assumes that the numbers of all conserved particle species are fixed.) We shall now assume that the reservoir has a quadratic entropy function. (This puts no restrictions on the barrier, whose entropy is assumed to be negligible.) For a quadratic reservoir, constant  $\mathbf{A}^0$  is equivalent to constant  $\bar{\beta}$ . We may thus use the expansion given by Eq. (6) in (19):

$$\int [(\alpha_r A_{jk} - \alpha_j A_{ik}) \Delta \beta_k + (\alpha_i B_{jklm} - \alpha_j B_{iklm}) \Delta \beta_k \Delta \beta_l \Delta \beta_m] e^S d^K \alpha = 0 \quad (20)$$

Making use of the facts that  $\Delta \beta_k e^S = \partial e^S / \partial \alpha_k$  and  $\partial^3 S / \partial \alpha_k \partial \alpha_l \partial \alpha_m = 0$  we can, by two partial integrations, write Eq. (20) in the form

$$\int [A_{ij} - A_{ji} + 3(B_{ijlm} - B_{jilm}) \sigma_{lm}] e^{S(\alpha)} d^K \alpha = 0 \quad (21)$$

where  $S(\alpha) = S(0) - \frac{1}{2} \sigma_{kl} \alpha_k \alpha_l$ . This implies that

$$A_{ij} - A_{ji} + 3(B_{ijlm} - B_{jilm}) \sigma_{lm} = 0 \quad (22)$$

We now recall that the barrier coefficients  $A_{ij}$  and  $B_{ijlm}$  are independent of the reservoir entropy function. If we were to replace the quadratic reservoir by another reservoir which, at the same value of  $\bar{\beta}$  had a quadratic expansion with coefficients  $\sigma'_{lm}$ , then Eq. (22) would remain valid with  $\sigma_{lm}$  replaced by  $\sigma'_{lm}$ . Thus the terms in Eq. (22) must be separately zero:

$$A_{ij} = A_{ji} \quad (23)$$

and

$$B_{ijkl} = B_{jikl} \quad (24)$$

Since, by its basic definition [Eq. (6)]  $B_{ijkl}$  is symmetric in the indices  $(j, k, l)$  the symmetry with respect to interchange of  $i$  and  $j$  shows that  $B_{ijkl}$  is completely symmetric. Eq. (23) is the conventional Onsager relations for this system in the linear flow approximation.<sup>(1,3)</sup>

## REFERENCES

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