

On the Microscopic Background of the Onsager–Casimir Reciprocity Relations

Urbaan M. Titulaer¹

Received April 7, 1988

It has been known for some time that small deviations from the Onsager–Casimir symmetry relations are introduced when one passes from a given description of a system to a less detailed one by adiabatic elimination of fast variables. Exact validity is preserved, however, for a slightly modified form of these relations. In this paper the question is considered whether this modified Onsager symmetry is also preserved by the transition from a microscopic to a mesoscopic description, the step that introduces manifest irreversibility into the equations of motion. This question is examined in detail for a system of a few heavy oscillators coupled to a bath, a model discussed in a recent paper by van Kampen. The modified Onsager symmetry survives the transition to an irreversible description via the dense spectrum approximation. This is shown explicitly by inspection of the results obtained by van Kampen; some arguments favoring a more general validity are also briefly discussed.

KEY WORDS: Onsager–Casimir symmetry; contracted description; coupled oscillator models; Liouville equation.

1. INTRODUCTION AND SURVEY

Onsager's reciprocity relations,⁽¹⁾ later extended by Casimir,⁽²⁾ express restrictions on the possible forms of macroscopic relaxation equations that follow from the time reversal invariance of the microscopic equations of motion. Onsager's derivation uses the famous *regression hypothesis*: he assumes that the fluctuations around equilibrium decay according to the macroscopic relaxation equations. Closer inspection of the proof shows that this requirement must be imposed for all times, whereas the validity of macroscopic relaxation equations is restricted to macroscopic time scales.

This paper is dedicated to Prof. Nico van Kampen.

¹ Institut für theoretische Physik, Johannes Kepler Universität Linz, A-4040 Linz, Austria.

As was first noted by McLennan,⁽³⁾ deviations at small times, so-called initial slip effects, should cause deviations from Onsager symmetry as well; these deviations were shown explicitly for the case of the linearized Burnett equations. Similar conclusions were reached by Geigenmüller *et al.*⁽⁴⁾ in an analysis of adiabatic elimination schemes: exact validity of Onsager symmetry on one level of description implies only approximate Onsager symmetry after the adiabatic elimination of fast variables. These authors also proposed a modification of the Onsager relations that allows them to survive the adiabatic elimination procedure.

The analysis in ref. 4 enables one to deduce the validity of the suitably modified Onsager relations on the macroscopic level when their validity on the mesoscopic level is assumed. This procedure was demonstrated in detail in two recent papers for the cases of the generalized Smoluchowski equation⁽⁵⁾ and of the linearized Burnett equations.⁽⁶⁾ This of course leaves the question of how to derive the mesoscopic Onsager symmetry from the microscopic equations of motion. Since there is no universal algorithm for deriving mesoscopic equations, the question can be answered only for special cases. In this paper I shall mainly discuss a coupled oscillator model (a number of heavy oscillators in a common bath) treated in a recent paper by van Kampen;⁽⁷⁾ his paper also contains a survey of earlier work on closely related models. The analysis will show that the modified Onsager symmetry proposed in ref. 4 is also valid on the mesoscopic level, at least for van Kampen's example.

It turns out to be convenient to focus attention not on the Onsager relations themselves, but on a mathematically equivalent property, a relation between the left and right eigenvectors of the evolution operator discussed by Felderhof and Titulaer.^(8,9) In Section 2, I establish this relation for the microscopic equation of motion, i.e., for the Liouville equation. Since van Kampen's Hamiltonian is not invariant under time reversal, I discuss the general case, already treated in ref. 9, where the Hamiltonian depends on some parameters odd under time reversal. The analysis closely follows the one in refs. 8 and 9, and it is mainly included to establish the notation and to make the paper reasonably self-contained.

In Section 3, I discuss the transition from the exact microscopic evolution to an effective irreversible evolution for positive times, and show that the symmetry property derived in Section 2 is preserved in this process. The explicit verification turns out to be particularly simple for van Kampen's choice of the Hamiltonian and the fundamental variables. In Section 4, I discuss the contraction of the description, in van Kampen's case by elimination of the bath variables. Formally, the steps to be taken are quite similar to those in ref. 4, but some care is needed in the interpretation of the formalism (transition from microscopic phase functions to

expectation values). Moreover, some modifications are needed due to the parameters in the Hamiltonian that are odd under time reversal. The final section contains a statement of the conclusions and some remarks and speculations about possible extensions to more general cases.

2. SYMMETRY PROPERTIES OF THE LIOUVILLE OPERATOR

Since the Liouville operator is a linear operator that correctly describes the time evolution of phase functions on all time scales, it is not surprising that it should obey exact Onsager–Casimir symmetry when the condition of (generalized) microscopic reversibility is fulfilled. However, in order to show this explicitly, one must first recast the Liouville equation as a set of coupled linear evolution equations for a set of phase functions; this form is obtained below in (2.7). I then show that the evolution matrix figuring in this set of equations obeys the relations (2.15) and (2.18) that were earlier shown⁽⁹⁾ to be equivalent to exact Onsager–Casimir symmetry. In the final part of the section I note some simple but useful corollaries. The results are not surprising physically, but I felt it necessary to present the derivation in some detail, since the formal point of view taken may not be too familiar. Most of the details of the formalism are not essential, however, for an understanding of the developments in the later sections of the paper.

The dynamics of the phase functions of a classical many-particle system, i.e., of the functions of coordinates and momenta $\{q_n\}$ and $\{p_n\}$,

$$g(\{p_n\}, \{q_n\}, t) \equiv g(\{p_n(t)\}, \{q_n(t)\}) \quad (2.1)$$

is governed by the Liouville equation

$$\frac{d}{dt} g = \{g, H(\mathbf{B})\} \equiv \mathcal{M}(\mathbf{B}) g \quad (2.2)$$

where $\{.,.\}$ denotes the Poisson bracket. The Hamilton function $H(\mathbf{B})$ of the system depends on some parameters B_k with odd time parity, such as magnetic fields or overall rotation velocities; they are denoted collectively by \mathbf{B} . The Liouville operator \mathcal{M} is anti-Hermitian with respect to the scalar product

$$\langle f, g \rangle_{E, \mathbf{B}} \equiv \langle f^* g \rangle_{mc, E} \quad (2.3)$$

where $\langle A \rangle_{mc, E}$ denotes the microcanonical average over the shell $H(\{p_n\}, \{q_n\}, \mathbf{B}) = E$. The eigenvalues μ_k of \mathcal{M} are purely imaginary and the corresponding eigenfunctions are orthogonal with respect to (2.3).

The abstract operator $\mathcal{M}(\mathbf{B})$ can be represented as an (infinite) matrix via the choice of a basis $e_i(\{p_n\}, \{q_n\})$ in the Hilbert space of phase functions with the scalar product (2.3). The e_i should be complete and independent; moreover, I require them to be real and to be eigenfunctions of the time-reversal operator \mathcal{U} defined via²

$$\mathcal{U}p_n = -p_n, \quad \mathcal{U}q_n = q_n \quad (2.4)$$

I do *not* require the $\{e_i\}$ to be orthogonal; their scalar products are denoted by

$$\langle e_i, e_j \rangle_{E, \mathbf{B}} \equiv [G(\mathbf{B})]_{ij}^{-1} \quad (2.5)$$

where I suppressed the dependence of \mathbf{G} on E . For a system with *simple microscopic reversibility*, i.e., invariance of the dynamics under (2.4), $[G(\mathbf{B})]_{ij}^{-1}$ should vanish when e_i and e_j have different time parity. For the case of *generalized microscopic reversibility*, i.e., invariance under (2.4) supplemented by inversion of the $\{B_k\}$, such matrix elements are allowed, but they should be odd in the $\{B_k\}$. This property is expressed compactly as

$$\mathbf{U} \cdot \mathbf{G}(\mathbf{B}) \cdot \mathbf{U} = \mathbf{G}(-\mathbf{B}) \quad (2.6)$$

where \mathbf{U} denotes the representation of the operator \mathcal{U} , i.e., $U_{ij} = \delta_{ij}\eta_j$, where $\eta_j = \pm 1$ is the time parity of e_j . In the chosen representation, (2.2) translates into a coupled set of equations for the $\{e_i(\{p_n\}, \{q_n\}, t)\}$:

$$\frac{d}{dt} e_i = \sum_j M(\mathbf{B})_{ij} e_j \quad (2.7)$$

with

$$\begin{aligned} M(\mathbf{B})_{ij} &= \sum_k [G(\mathbf{B})]_{jk}^{-1} \langle e_k, \mathcal{M}(\mathbf{B}) e_i \rangle_{E, \mathbf{B}} \\ &= -\sum_k \langle e_i, \mathcal{M}(\mathbf{B}) e_k \rangle_{E, \mathbf{B}} [G(\mathbf{B})]_{kj}^{-1} \end{aligned} \quad (2.8)$$

If one denotes the eigenfunction of \mathcal{M} with eigenvalue μ_k by

$$\tilde{f}(\mathbf{B})^k(\{p_n\}, \{q_n\}) = \sum_i \tilde{f}(\mathbf{B})_i^k e_i(\{p_n\}, \{q_n\}) \quad (2.9)$$

² Physically, it makes more sense to define time reversal in terms of a sign change of the velocities rather than the momenta; this will be accomplished, however, by the generalized time reversal to be discussed presently.

then the corresponding eigenvector of $M(\mathbf{B})$ is

$$f(\mathbf{B})_i^k = \sum_j G(\mathbf{B})_{ij} \tilde{f}(\mathbf{B})_j^k \quad (2.10)$$

and the orthogonality of the functions (2.9) translates into

$$\sum_{ij} f(\mathbf{B})_i^{k*} G(\mathbf{B})_{ij} f(\mathbf{B})_j^l = \delta_{kl} \quad (2.11)$$

This relation and the symmetry of $G(\mathbf{B})$ imply that $G(\mathbf{B}) \cdot \mathbf{f}(\mathbf{B})^{k*}$ is the *left* eigenvector of $M(\mathbf{B})$ with eigenvalue μ_k . Note, however, that, due to the reality of $M(\mathbf{B})$, the vector $\mathbf{f}(\mathbf{B})^{k*}$ is also an eigenvector of $M(\mathbf{B})$, with eigenvalue $\mu_k^* = -\mu_k$. To obtain a relation between left and right eigenvectors belonging to the same eigenvalue, one may exploit the relation

$$\mathcal{U} M(\mathbf{B}) \mathcal{U} = -M(-\mathbf{B}) \quad (2.12)$$

which follows from generalized microscopic reversibility. This relation, together with (2.6) and (2.8), implies

$$M(-\mathbf{B}) \cdot \mathbf{U} \cdot \mathbf{f}(\mathbf{B})^{k*} = +\mu_k \mathbf{U} \cdot \mathbf{f}(\mathbf{B})^{k*} \quad (2.13)$$

Thus, a possible choice for the eigenvector of $M(-\mathbf{B})$ to the eigenvalue μ_k is

$$\mathbf{f}(-\mathbf{B})^k = -\mathbf{U} \cdot \mathbf{f}(\mathbf{B})^{k*} \quad (2.14)$$

where the minus sign is purely conventional. The relation (2.11) can now be rewritten as a *real* biorthonormality property between the right eigenvectors of $M(\mathbf{B})$ and $M(-\mathbf{B})$:

$$\mathbf{f}(-\mathbf{B})^k \cdot \hat{G}(\mathbf{B}) \cdot \mathbf{f}(\mathbf{B})^l = \delta_{kl} \quad (2.15)$$

with the indefinite “weight matrix”

$$\hat{G}(\mathbf{B}) = -\mathbf{U} \cdot G(\mathbf{B}) \quad (2.16)$$

The *left* eigenvector of $M(-\mathbf{B})$ to the eigenvalue μ_k is now given by

$$-G(-\mathbf{B}) \cdot \mathbf{U} \cdot \mathbf{f}(\mathbf{B})^k = -\mathbf{U} \cdot G(\mathbf{B}) \cdot \mathbf{f}(\mathbf{B})^k = \hat{G}(\mathbf{B}) \cdot \mathbf{f}(\mathbf{B})^k \quad (2.17)$$

where I used the relation between left and right eigenvectors derived from (2.11), as well as (2.6). Thus, the matrix $\hat{G}(\mathbf{B})$ transforms a right eigenvector of $M(\mathbf{B})$ into a left eigenvector of $M(-\mathbf{B})$ to the same eigenvalue.

The transposed matrix $M(-\mathbf{B})^T$ is therefore connected with $M(\mathbf{B})$ by the similarity transformation

$$M(-\mathbf{B})^T = \hat{\mathbf{G}}(\mathbf{B}) \cdot M(\mathbf{B}) \cdot \hat{\mathbf{G}}(\mathbf{B})^{-1} \quad (2.18)$$

Since the relation (2.18) was shown^(8,9) to be equivalent to Onsager–Casimir symmetry, I shall occasionally call (2.18) the Onsager–Casimir symmetry property. The matrix $\hat{\mathbf{G}}(\mathbf{B})$ is in general not symmetric; from (2.6) and the symmetry of $\mathbf{G}(\mathbf{B})$, apparent from (2.5), one finds

$$\hat{\mathbf{G}}(\mathbf{B})^T = \hat{\mathbf{G}}(-\mathbf{B}) \quad (2.19)$$

a relation that resolves the apparent asymmetry between \mathbf{B} and $-\mathbf{B}$ in (2.15).

The similarity relation (2.18) also holds for any function of the matrix $M(\mathbf{B})$, such as the evolution matrix

$$T(t; \mathbf{B}) = \exp[M(\mathbf{B}) t] \quad (2.20)$$

and the resolvent

$$R(z; \mathbf{B}) \equiv [z - M(\mathbf{B})]^{-1} \quad (2.21)$$

and in particular also for all spectral projections, which can be obtained from $R(z; \mathbf{B})$ by contour integration.⁽¹⁰⁾

3. IRREVERSIBILITY AND QUASIEIGENVECTORS OF THE LIOUVILLE OPERATOR

There is no generally applicable algorithm that allows one to derive a closed macroscopic or mesoscopic description of a system from the microscopic dynamics governed by the Liouville equation. Therefore, one should not expect to find a general scheme for deriving mesoscopic or macroscopic Onsager–Casimir symmetry relations from the microscopic ones discussed in the preceding section. For many systems one may derive or justify a coarse-grained description by means of a master equation. For closed systems with microscopic reversibility the transition kernel \mathcal{W} occurring in the master equation satisfies (extended) detailed balance properties⁽¹¹⁾ that lead to relations between left and right eigenfunctions of the master operator quite similar to those just discussed for the case of the Liouville operator. For two special master equations, the Klein–Kramers equation and the linearized Boltzmann equation, these relations were discussed in detail by Hubmer and Titulaer.^(5,6) For systems with parameters \mathbf{B} odd under time reversal that obey generalized microscopic time-reversal

symmetry one may similarly derive relations between the master operators $\mathcal{W}(\mathbf{B})$ and $\mathcal{W}(-\mathbf{B})$ from which relations between the left eigenfunctions of the one and the right eigenfunctions of the other may be deduced. In all these cases the detailed balance-type properties of \mathcal{W} are derived directly from the microscopic reversibility requirements, and the symmetry properties of the Liouville operator do not enter as such into the argument.

For some special systems, however, the reasons for the appearance of irreversible behavior can be analyzed in more detail. The example treated most completely consists of an assembly of linearly coupled harmonic oscillators: a number of heavy oscillators are coupled weakly to a large number of bath oscillators. A recent discussion of such a system was given by van Kampen⁽⁷⁾; he considered heavy oscillators with annihilation “operators” A_r and bath oscillators with annihilation “operators” a_k governed by the Hamiltonian

$$H = \sum_r \Omega_r A_r^* A_r + \sum_k k a_k^* a_k + \sum_{rk} (v_{rk} A_r^* a_k + v_{rk}^* A_r a_k^*) \quad (3.1)$$

(I consider only the classical version of this system; the annihilation “operators” are defined by

$$A_r \equiv \frac{1}{\sqrt{2}} \left[(M_r \Omega_r)^{1/2} Q_r + \frac{i}{(M_r \Omega_r)^{1/2}} P_r \right] \quad (3.2)$$

etc., and their complex conjugates are denoted by A_r^* rather than A_r^\dagger .) Since time reversal amounts to complex conjugation of the A_r and a_k , the Hamiltonian (3.1) is not invariant unless one requires the imaginary parts of the v_{rk} to change sign under time reversal as well; the latter therefore play the role of the \mathbf{B} in Section 2.

Van Kampen shows that for a sufficiently dense spectrum of the bath oscillators⁽¹²⁾ (and for a sufficiently smooth dependence of the v_{rk} on k) the action of the evolution operator $\mathbb{T}(t; \{v_{rk}\})$ for the A_r and a_k can be mimicked for $t > 0$ by an effective evolution operator of the form

$$\mathbb{T}_{\text{eff}}(t) = \sum_r C_r e^{-iA_r t} + \sum_k C_k e^{-ik t} \quad (3.3)$$

with *complex* frequencies A_r (with negative imaginary parts). Explicit approximate expressions are given for the C_r and the C_k for the case of two heavy oscillators with equal Ω_r . It seems reasonable to expect that the symmetry properties of type (2.18) transfer from $\mathbb{T}(t; \{v_{rk}\})$ to $\mathbb{T}_{\text{eff}}(t; \{v_k\})$, and hence to the quasieigenprojectors C_r and C_k . This in turn would imply Onsager symmetry for the effective evolution operator

$$\mathbb{M}_{\text{eff}}(t) = -\sum_r i A_r C_r - \sum_k i k C_k \quad (3.4)$$

For the system described by (3.1) the symmetry (2.18) takes a particularly simple form. Both \mathbf{M} and \mathbf{G} for the subspace of phase functions spanned by the annihilation operators and their complex conjugates can be expressed in terms of the coefficient matrix of H :

$$\mathbf{H} = \begin{pmatrix} \Omega_r \delta_{rr'} & v_{rk'} \\ v_{r'k}^* & k \delta_{kk'} \end{pmatrix} \quad (3.5)$$

The respective expressions are

$$\mathbf{M} = \begin{pmatrix} -i\mathbf{H} & \mathbf{0} \\ \mathbf{0} & i\mathbf{H}^T \end{pmatrix}, \quad \mathbf{G} = \frac{1}{2kT} \begin{pmatrix} \mathbf{H} & \mathbf{0} \\ \mathbf{0} & \mathbf{H}^T \end{pmatrix} \quad (3.6)$$

(the block notation refers to the $\{A_r, a_k\}$ and $\{A_r^*, a_k^*\}$ subspaces). The expression for \mathbf{G} was calculated with a canonical instead of a microcanonical average, which is justified for a large system. Hence, for our system, and in the chosen representation, the matrices \mathbf{G} and \mathbf{M} commute and the Onsager–Casimir symmetry requirement (2.18) becomes

$$\mathcal{T}[\mathbf{M}(\{v_{rk}^*\})] = \mathbf{U} \cdot \mathbf{M}(\{v_{rk}\}) \cdot \mathbf{U} \quad (3.7)$$

where $\mathcal{T}[\mathbf{C}]$ denotes the operation corresponding to matrix transposition in a real representation. As I shall show in the Appendix, this operation in the complex representation used in ref. 7 amounts, for the matrices considered, to transposition plus sandwiching between \mathbf{U} matrices. Hence, the condition (3.7) in complex representation reads

$$\mathbf{M}(\{v_{rk}^*\})^T = \mathbf{M}(\{v_{rk}\}) \quad (3.8)$$

which is clearly satisfied due to the Hermiticity of \mathbf{H} , which contains no complex numbers except the $\{v_{rk}\}$. The form (3.8) for the relation (2.18) holds equally for any function of \mathbf{M} , and in particular for its spectral projectors. The quasidegenprojections (3.4), as calculated explicitly by van Kampen, are no longer Hermitian; they do, however, turn out to satisfy (i stands for r or k)

$$\mathbf{C}_i(\{v_{rk}\}) = \mathbf{C}_i(\{v_{rk}^*\})^T \quad (3.9)$$

[In verifying this result, one should note that the quantity γ in Eqs. (34)–(38) of ref. 7 is defined in (29) of that work as the phase of the average value of $v_{1k} v_{2k}^*$ around $k = \Omega$, and hence changes sign when the v_{rk} are replaced by their complex conjugates. The imaginary parts of the A_r , however, do not change under this replacement.] Thus, the conjecture about the preservation of the symmetry (2.18) during the transition to the

effective Liouville operator can be verified for van Kampen’s example. This is not completely unexpected, since the quasieigenprojectors may be considered as the residues of poles in the analytic continuation of the resolvent $R(z) = [z - M]^{-1}$ across the cut that evolves^(12,18) from the alternation of poles and zeros on the imaginary z axis in the dense spectrum limit. Since $R(z)$ satisfies the Onsager–Casimir symmetry (2.18) throughout the physical sheet, it should retain this property upon analytic continuation.

The explicit construction of the quasieigenprojectors in van Kampen’s example relies heavily on the special properties of the coupled oscillator system. On the other hand, quasimodes of the Liouville operator with complex frequencies are widely discussed in the literature; they play an essential part in the Mori–Zwanzig projection operator formalism.⁽¹³⁾ If the picture of two evolution operators $T(t)$ and $T_{\text{eff}}(t)$ that describe practically indistinguishable evolutions for $t > 0$, and hence have practically indistinguishable resolvents for $\text{Re } z > 0$, is more generally valid, then a mechanism for the transference of Onsager–Casimir symmetry from $T(t)$ to $T_{\text{eff}}(t)$ immediately suggests itself. Note, however, that $T_{\text{eff}}(t)$ is still an evolution operator in the full phase space of the system (or in some invariant subspace containing phase functions related to all degrees of freedom). The fate of the symmetry relations under a contraction of the description will be discussed in a slightly broader context in the next section.

4. SYMMETRY PROPERTIES OF REDUCED EVOLUTION OPERATORS

In the two preceding sections I considered the dynamics in the Hilbert space of phase functions. The equations that describe the time dependence of the phase functions also describe the evolution of their expectation values for a distribution $f(\{p_n\}, \{q_n\})$ of the coordinates and momenta,

$$\langle e_i \rangle_f(t) = \int d\{p_n\} d\{q_n\} f(\{p_n\}, \{q_n\}) e_i(\{p_n\}, \{q_n\}, t) \quad (4.1)$$

The set of equations for the $\langle e_i \rangle_f$ can be simplified if one succeeds in choosing the e_i in such a way that the first k of them have only small components outside of the range of a k -dimensional spectral projector \mathcal{P} in the Hilbert space that corresponds to a spectral projector \mathbf{P} of the evolution matrix \mathbf{M} or \mathbf{M}_{eff} .³ One may then decompose f according to

$$f = f_0 + f_1; \quad f_0 = \mathcal{P}f \quad (4.2)$$

³ I shall temporarily omit the argument \mathbf{B} or $-\mathbf{B}$.

and the expectation values $\langle e_i \rangle$ accordingly as

$$\langle e_i \rangle_f(t) = \langle e_i \rangle_0(t) + \langle e_i \rangle_1(t) \quad (4.3)$$

For the purpose of calculating the $\langle e_i \rangle_0(t)$ one may treat the e_i with $i > k$, denoted collectively as \mathbf{y} , as linear combinations of the e_i with $i \leq k$, denoted collectively as \mathbf{x} ; from

$$\begin{pmatrix} \langle \mathbf{x} \rangle_0 \\ \langle \mathbf{y} \rangle_0 \end{pmatrix} = \begin{pmatrix} \mathbf{P}_{xx} & \mathbf{P}_{xy} \\ \mathbf{P}_{yx} & \mathbf{P}_{yy} \end{pmatrix} \begin{pmatrix} \langle \mathbf{x} \rangle_0 \\ \langle \mathbf{y} \rangle_0 \end{pmatrix} \quad (4.4)$$

where \mathbf{P}_{xx} , etc., are appropriate submatrices of \mathbf{P} , one concludes

$$\langle \mathbf{y} \rangle_0 = [\mathbf{1} - \mathbf{P}_{yy}]^{-1} \cdot \mathbf{P}_{yx} \cdot \langle \mathbf{x} \rangle_0 \equiv \mathbf{R} \cdot \langle \mathbf{x} \rangle_0 \quad (4.5)$$

The matrix \mathbf{R} was designated as the reconstruction matrix⁽¹⁴⁾ (or operator). The evolution of the $\langle \mathbf{x} \rangle_0$ follows from

$$\frac{d}{dt} \begin{pmatrix} \langle \mathbf{x} \rangle_0 \\ \mathbf{R} \cdot \langle \mathbf{x} \rangle_0 \end{pmatrix} = \begin{pmatrix} \mathbf{M}_{xx} & \mathbf{M}_{xy} \\ \mathbf{M}_{yx} & \mathbf{M}_{yy} \end{pmatrix} \begin{pmatrix} \langle \mathbf{x} \rangle_0 \\ \mathbf{R} \cdot \langle \mathbf{x} \rangle_0 \end{pmatrix} \quad (4.6)$$

where \mathbf{M}_{xx} , etc., are the appropriate submatrices of \mathbf{M} or \mathbf{M}_{eff} . The first row of this matrix equation yields a closed evolution equation for $\langle \mathbf{x} \rangle_0$:

$$\frac{d}{dt} \langle \mathbf{x} \rangle_0 = (\mathbf{M}_{xx} + \mathbf{M}_{xy} \cdot \mathbf{R}) \cdot \langle \mathbf{x} \rangle_0 \equiv \mathbf{M}_{\text{red}} \cdot \langle \mathbf{x} \rangle_0 \quad (4.7)$$

while the second row yields the consistency condition

$$\mathbf{R} \cdot \mathbf{M}_{\text{red}} = \mathbf{M}_{yx} + \mathbf{M}_{yy} \cdot \mathbf{R} \quad (4.8)$$

that may be used, together with the definition of \mathbf{M}_{red} in (4.7), to determine \mathbf{R} perturbatively. The quantities \mathbf{M}_{yx} and \mathbf{M}_{xy} are small by construction; if one assumes \mathbf{M}_{xx} to be small as well, one obtains the algorithm for the adiabatic elimination of fast variables⁽¹⁵⁾; when both \mathbf{M}_{xx} and \mathbf{M}_{yy} are assumed to be of order unity, one obtains a variant of the perturbation theory familiar from quantum mechanics⁴; when \mathbf{M}_{yy} is treated as small, one obtains a dynamics for fast variables (at virtually constant values of the slow variables) considered by Geigenmüller *et al.*⁽¹⁷⁾

As in refs. 4–6, I shall now deduce orthogonality properties between the eigenvectors of $\mathbf{M}_{\text{red}}(\mathbf{B})$ and $\mathbf{M}_{\text{red}}(-\mathbf{B})$ from those between the eigenvectors of $\mathbf{M}(\mathbf{B})$ and $\mathbf{M}(-\mathbf{B})$, or of their effective counterparts. From the

⁴ More specifically: a variant of this formalism discussed by Bloch⁽¹⁶⁾ and Kato,⁽¹⁰⁾ generalized from single eigenvalues to groups of eigenvalues.

construction of $M_{\text{red}}(\mathbf{B})$ it follows that its eigenvectors $\mathbf{x}(\mathbf{B})^k$ are just the \mathbf{x} parts of those eigenvectors $\mathbf{f}(\mathbf{B})^k$ of $M(\mathbf{B})$ or $M_{\text{eff}}(\mathbf{B})$ on which the projector $P(\mathbf{B})$ projects. From the orthogonality relation (2.15), which is preserved by the transition to $M_{\text{eff}}(\mathbf{B})$, one sees that

$$\begin{pmatrix} \mathbf{x}(-\mathbf{B})^k \\ \mathbf{R} \cdot \mathbf{x}(-\mathbf{B})^k \end{pmatrix}^T \cdot \begin{pmatrix} \hat{\mathbf{G}}(\mathbf{B})_{xx} & \hat{\mathbf{G}}(\mathbf{B})_{xy} \\ \hat{\mathbf{G}}(\mathbf{B})_{yx} & \hat{\mathbf{G}}(\mathbf{B})_{yy} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{x}(\mathbf{B})^l \\ \mathbf{R} \cdot \mathbf{x}(\mathbf{B})^l \end{pmatrix} = \delta_{kl} \quad (4.9)$$

which can be written as

$$\mathbf{x}(-\mathbf{B})^k \cdot \hat{\mathbf{G}}(\mathbf{B})_{\text{red}} \cdot \mathbf{x}(\mathbf{B})^l = \delta_{kl} \quad (4.10)$$

with a reduced $\hat{\mathbf{G}}$ matrix defined as

$$\begin{aligned} \hat{\mathbf{G}}(\mathbf{B})_{\text{red}} &= \hat{\mathbf{G}}(\mathbf{B})_{xx} + \hat{\mathbf{G}}(\mathbf{B})_{xy} \cdot \mathbf{R}(\mathbf{B}) \\ &\quad + \mathbf{R}(-\mathbf{B})^T \cdot \hat{\mathbf{G}}_{yx}(\mathbf{B}) \\ &\quad + \mathbf{R}(-\mathbf{B})^T \cdot \hat{\mathbf{G}}_{yy}(\mathbf{B}) \cdot \mathbf{R}(\mathbf{B}) \end{aligned} \quad (4.11)$$

From the relation (4.10) between the eigenvectors, analogous to (2.15), one immediately derives the analog of (2.18),

$$\mathbf{M}(-\mathbf{B})_{\text{red}}^T = \hat{\mathbf{G}}(\mathbf{B})_{\text{red}} \cdot \mathbf{M}(\mathbf{B})_{\text{red}} \cdot \hat{\mathbf{G}}(\mathbf{B})_{\text{red}}^{-1} \quad (4.12)$$

Similarly, the analog of (2.19),

$$\hat{\mathbf{G}}(-\mathbf{B})_{\text{red}}^T = \hat{\mathbf{G}}(\mathbf{B})_{\text{red}} \quad (4.13)$$

follows directly from (2.19) and (4.11). Thus, the modified Onsager–Casimir symmetry survives the transition to a reduced dynamics.

Thus far I have merely shown the symmetry properties for the dynamics of the rather formally defined objects $\langle \mathbf{x} \rangle_0(t)$. Whether and when they correspond to the physically observed quantities $\langle \mathbf{x} \rangle(t) \equiv \langle \mathbf{x} \rangle_0(t) + \langle \mathbf{x} \rangle_1(t)$ depends on the physics of the case considered. When there is a difference in orders of magnitude between the eigenvalues on which P projects and the remaining ones, the part $\langle \mathbf{x} \rangle_0(t)$ dominates either the initial or the long-time part of $\langle \mathbf{x} \rangle(t)$ (after time smoothing if the large eigenvalues are purely imaginary). This is the adiabatic elimination case extensively discussed elsewhere.⁽⁴⁻⁶⁾ For the example discussed in the preceding section, one may choose for P the projection on the quasideigenvectors associated with the complex eigenvalues of M_{eff} , and for the e_i the coordinates and momenta of the heavy oscillators. For this case the $\langle \mathbf{x} \rangle_1(t)$ contain the contributions of the continuous spectrum of M_{eff} to the dynamics, as well as the error terms involved in the transition from M to M_{eff} . A careful discussion of these terms for a single heavy

oscillator was given by Ullersma^{(18),5}; it turns out that $\langle \mathbf{x} \rangle_1(t)$ is negligible, except at small times, where there are transients that depend on the bath size, and at very large times, after the $\langle \mathbf{x} \rangle_0(t)$ have almost died out. (At least, this is the case for “reasonable” distributions of coordinates and momenta of the bath oscillators, and in particular if the latter are in thermal equilibrium.) The matrix M_{red} also governs the decay of the thermal fluctuations of the \mathbf{x} , again up to transients and large time contributions, since these may be expressed as expectation values of the x_i for distributions $x_j f_{\text{eq}}$. These distributions do not lie completely within the range of P , hence the autocorrelation functions in general will have transient contributions.

5. CONCLUDING REMARKS

The main result of this paper is the preservation of the weighted orthogonality relation (2.15) or the similarity relation (2.18) under a number of procedures involved in the transition from a microscopic to a mesoscopic or macroscopic description: the transition to an effective, irreversible evolution by means of the dense spectrum approximation and the elimination of certain of the variables from the description. In the course of the latter procedure the matrix \hat{G} is replaced by a matrix \hat{G}_{red} in the reduced variable space. The simple relation (2.16) between \hat{G} and the matrix G that occurs in the expression for the equal-time correlations is thereby destroyed; the reduced G matrix formed in analogy with (4.11) would be

$$G(\mathbf{B})_{\text{red}} = G(\mathbf{B})_{xx} + G(\mathbf{B})_{xy} \cdot R(\mathbf{B}) + R(\mathbf{B})^T \cdot G(\mathbf{B})_{yx} + R(\mathbf{B})^T \cdot G(\mathbf{B})_{yy} \cdot R(\mathbf{B}) \quad (5.1)$$

Physically, $\mathbf{x} \cdot G_{\text{red}} \cdot \mathbf{x}$ is, up to a factor, the entropy (or free energy) content of a deviation from equilibrium *completely within the P subspace* characterized by the main components \mathbf{x} .^(4,6) However, as was shown in refs. 4–6, it is \hat{G}_{red} rather than G_{red} that determines the back-extrapolated initial values of the P part of the autocorrelation function, and hence may be measured in favorable cases by scattering experiments.⁽³⁾ The relation (2.16) holds for the leading terms in G_{red} and \hat{G}_{red} , but not in general for the correction terms. The relation (2.16) is the condition for the equivalence of the relations (2.15) or (2.18) to the conventional Onsager–Casimir relations, as is discussed more fully in refs. 4–6. The correction terms, however, all involve, via R , the small coupling between eliminated and retained variables. Furthermore, the quantities G_{xy} and G_{yx} are often small of the same order (as in van Kampen’s example), or can be made small by a transformation of variables.⁽¹⁷⁾ Thus, the difference

⁵ A similar analysis for a many-oscillator case was given by Ullersma and Tjon.⁽¹⁹⁾

between modified and orthodox Onsager–Casimir relations in general becomes apparent only in correction terms of second order in the smallness parameter.

The derivations given in this paper are not optimal with respect to generality and mathematical rigor. The assumption of a discrete spectrum for the Liouville operator \mathcal{M} , necessary for the existence of normalizable eigenvectors, can certainly be avoided at the cost of a somewhat more awkward formulation; the essential relation (2.18) can then be proved from the analog of (2.13) for spectral measures. The modifications needed for the case of multiple nonsemisimple eigenvalues (i.e., for matrices that can only be brought into the Jordan normal form) were already discussed in ref. 9.

More serious mathematical issues are involved in the transition from $T(t)$ to $T(t)_{\text{eff}}$ in Section 3. Van Kampen's calculation shows that each matrix element of the first matrix approaches the corresponding element of the second one; the conclusions drawn about convergence of the spectral decompositions would require certain uniformity conditions, in t as well as in k , for the rate of convergence of the matrix elements, and hence some additional boundedness and regularity conditions on the coupling constants and the density of the bath oscillators as a function of k . Also, the quasideigenvalues λ_i and the parts of the associated eigenvectors in the heavy-oscillator subspace are calculated in ref. 7 only to the lowest non-trivial order in the couplings; calculations of higher order corrections for some special case would certainly be desirable as a further check on the general ideas in Section 3.

The most serious restriction of our discussion is its essential use of the linearity of the evolution equations on all levels of description. Purely formally, linearity can always be maintained by keeping the number of variables sufficiently large, and in most cases infinite. A treatment of mode coupling effects by means of such a formally linear theory was developed by Machta and Oppenheim.⁽²⁰⁾ It would be interesting to see whether a study of the Onsager symmetry of such extended schemes could lead to restrictions on the structure of higher order corrections to nonlinear evolution equations. Generalizations of the Onsager relations to certain nonlinear systems were considered in the context of a Fokker–Planck description in Chapter X of ref. 11.

APPENDIX

In the complex $(\mathbf{A}, \mathbf{A}^*)$ representation used in Section 3 the matrices \mathbf{M} and \mathbf{M}_{eff} (and all functions of these matrices) have the form

$$\mathbf{D}^c = \begin{pmatrix} \mathbf{D} & 0 \\ 0 & \mathbf{D}^* \end{pmatrix} \quad (\text{A.1})$$

An associated real representation can be obtained via the transformation

$$Q_i = \frac{1}{\sqrt{2}} (A_i + A_i^*), \quad P_i = \frac{1}{i\sqrt{2}} (A_i - A_i^*) \quad (\text{A.2})$$

In the (\mathbf{Q}, \mathbf{P}) basis the representation of the matrix (A.1) is

$$D^r = \begin{pmatrix} D' & -D'' \\ D'' & D' \end{pmatrix} \quad (\text{A.3})$$

where D' and D'' stand for the real and imaginary parts, respectively, of the matrix D in (A.1). Transposition of D^r implies

$$D' \rightarrow (D')^T, \quad D'' \rightarrow -(D'')^T, \quad D \rightarrow (D^*)^T \quad (\text{A.4})$$

The complex conjugation can be removed by a time reversal transformation, which exchanges \mathbf{A} and \mathbf{A}^* :

$$(D^r)^T \Leftrightarrow \mathbf{U} \cdot (D^c)^T \cdot \mathbf{U} \equiv \mathcal{T}[D^c] \quad (\text{A.5})$$

This relation proves the equivalence of (3.7) and (3.8).

ACKNOWLEDGMENTS

I am grateful for a number of pleasant and stimulating discussions with Prof. Nico van Kampen over the last few years on subjects touched upon in this paper. I thank Dr. Harald Iro for helpful comments on an earlier draft of the manuscript.

REFERENCES

1. L. Onsager, *Phys. Rev.* **37**:405 (1931); **38**:2265 (1931).
2. H. B. G. Casimir, *Rev. Mod. Phys.* **17**:343 (1945).
3. J. A. McLennan, *Phys. Rev. A* **10**:1272 (1974).
4. U. Geigenmüller, U. M. Titulaer, and B. U. Felderhof, *Physica* **119A**:53 (1983).
5. G. F. Hubmer and U. M. Titulaer, *J. Stat. Phys.* **49**:331 (1987).
6. G. F. Hubmer and U. M. Titulaer, *J. Stat. Phys.* **50**:913 (1988).
7. N. G. van Kampen, *Physica* **147A**:165 (1987).
8. B. U. Felderhof and U. M. Titulaer, *Physica* **100A**:563 (1980).
9. U. M. Titulaer and B. U. Felderhof, *Physica* **100A**:573 (1980).
10. T. Kato, *Perturbation Theory for Linear Operators*, 2nd ed. (Springer, Berlin, 1976).
11. N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981), Chapter V.
12. N. G. van Kampen, *Dan. Mat. Fys. Medd.* **26**(15) (1951).

13. H. Mori, *Prog. Theor. Phys.* **34**:423 (1965); R. Zwanzig, *Lectures in Theoretical Physics*, Vol. 3 (Wiley, New York, 1961).
14. U. M. Titulaer, *Physica* **100A**:234 (1980).
15. U. Geigenmüller, U. M. Titulaer, and B. U. Felderhof, *Physica* **119A**:41 (1983).
16. C. Bloch, *Nucl. Phys.* **6**:329 (1958).
17. U. Geigenmüller, U. M. Titulaer, and B. U. Felderhof, *Physica* **120A**:635 (1983).
18. P. Ullersma, *Physica* **32**:27, 56, 74, 90 (1966).
19. P. Ullersma and J. A. Tjon, *Physica* **71**:294 (1974).
20. J. Machta and I. Oppenheim, *Physica* **112A**:361 (1982).