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The Onsager–Casimir Relations Revisited

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We study the fate of the Onsager–Casimir reciprocity relations for a continuous system when some of its variables are eliminated adiabatically. Just as for discrete systems, deviations appear in correction terms to the reduced evolution equation that are of higher order in the time scale ratio. The deviations are not removed by including correction terms to the coarse-grained thermodynamic potential. However, via a reformulation of the theory, in which the central role of the thermodynamic potential is taken over by an associated Lagrangian-type expression, we arrive at a modified form of the Onsager–Casimir relations that survives the adiabatic elimination procedure. There is a simple relation between the time evolution of the redefined thermodynamic forces and that of the basic thermodynamic variables; this relation also survives the adiabatic elimination. The formalism is illustrated by explicit calculations for the Klein–Kramers equation, which describes the phase space distribution of Brownian particles, and for the corrected Smoluchowski equation derived from it by adiabatic elimination of the velocity variable. The symmetry relation for the latter leads to a simple proof that the reality of the eigenvalues of the simple Smoluchowski equation is not destroyed by the addition of higher order corrections, at least not within the framework of a formal perturbation expansion in the time scale ratio.

KEY WORDS: Onsager–Casimir relations; adiabatic elimination; Chapman–Enskog procedure; Brownian motion; Kramers equation; Smoluchowski equation; thermodynamic forces.

1. INTRODUCTION

The Onsager–Casimir reciprocity relations$^{(1-4)}$ express an important consequence of microscopic time-reversal invariance for the relaxation of macroscopic quantities in the linear regime close to thermodynamic equilibrium. The proof of these relations involves the assumption that the

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correlation functions for the thermal fluctuations of macroscopic quantities decay according to the macroscopic relaxation equations. Since the very concept of a closed system of equations for the macroscopic quantities alone contains approximations, this so-called regression hypothesis, and hence the Onsager–Casimir relations, can also have only approximate validity, though the approximation is in general an excellent one.

Closed equations for the macroscopic variables, which are almost by definition slowly varying ones, can be obtained by adiabatic elimination of all faster variables (see Ref. 5 for a survey). The equations thus derived are valid only asymptotically for times large compared to the fast frequencies and relaxation times. The initial conditions to be used with these equations are not simply the values of the macroscopic quantities in the microscopic initial state (or, for correlation functions, the equal-time correlation functions); there are correction terms of higher order in the time scale ratio. These so-called initial slip effects(6–8),2 are ultimately responsible for violations of the Onsager–Casimir relations, as was shown by Geigenmüller *et al.*(9) for systems with a finite number of macroscopic variables. In the present paper we shall extend the treatment of Ref. 9 to the case where the macroscopic quantities are fields, i.e., functions of space.

An explicit, systematic elimination of fast variables is possible only when the dynamics on the fast time scale is sufficiently simple. Hence, merely formal results can be expected from elimination schemes starting directly from the microscopic equations. More progress is possible when an intermediate, or mesoscopic, level is interposed. Then the transition from the microscopic to the mesoscopic level may still involve uncontrollable approximations, but the transition from the mesoscopic to the macroscopic one can be performed in a systematic way (at least for sufficiently simple mesoscopic equations) by means of the Chapman–Enskog algorithm.(6–8) The most important example of a tractable mesoscopic equation is the Boltzmann equation, for which the Chapman–Enskog method successively yields the Euler, Navier–Stokes, and Burnett equations. An even simpler case is the Klein–Kramers equation for the phase space distribution of a Brownian particle, from which the Smoluchowski equation and successive corrections to it are obtained.(7,8) The analogy with the finite-dimensional case(9) leads one to expect deviations from Onsager–Casimir symmetry in the higher order corrections obtained by the Chapman–Enskog method.

In continuous systems the familiar Onsager symmetry properties of the matrix connecting the fluxes (i.e., the time derivatives of the macroscopic quantities) with the thermodynamic forces (i.e., the derivatives of the thermodynamic potential) translate into Hermiticity properties of linear

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[2] See Ref. 6 for a modern treatment and references to the original literature.

operators, or operator-valued matrices. (The conventional Onsager relations for continuous systems can be deduced from these operator relations by specializing to simple geometries and boundary conditions, as is shown in detail, e.g., in Chapter VII of Ref. 3). In Section 2 we formulate the Hermiticity requirements explicitly. We then show that they are fulfilled by the operator occurring in the Klein–Kramers equation, or rather in a system of coupled moment equations equivalent to it. Analogous properties hold for the operator occurring in the Smoluchowski equation, as well as for the first correction to it, but not for the second correction term, as is shown in Section 3.

This violation of the Onsager property is not too surprising: it is certainly inconsistent to consider higher order corrections to the time evolution of the macroscopic quantities, but not to the free energy of the system, and hence to the expressions for the thermodynamic forces. However, correcting for this omission does not restore the Onsager property, as is also shown explicitly in Section 3.

The Onsager–Casimir symmetry relations can nevertheless be salvaged, but this requires a different definition of the thermodynamic forces: instead of the (functional) derivatives of the thermodynamic potential, in our case the free energy, one has to take those of an associated "thermodynamic Lagrangian," defined as the difference between the free energy contributions from macroscopic variables odd under time reversal and those from variables even under time reversal. This construction is carried out in Section 4. The distinct role played by the thermodynamic Lagrangian is closely related to a property noted by Felderhof and Titulaer(10): unlike the thermodynamic potential itself, the Lagrangian can be written as a sum of contributions from each of the normal modes of the evolution operator. In particular, there are no interference terms between normal, or Chapman–Enskog type, solutions of the mesoscopic equation on the one hand, and the rapidly decaying solutions that lead to the initial slip on the other hand. In the second half of Section 4 we show that the modified Onsager–Casimir relations allow one to draw much the same type of conclusions that are usually drawn from the classical ones. In particular, they provide a simple relation between the left and right eigenfunctions of the corrected Smoluchowski operator (cf. Refs. 10 and 11). They also lead to a formal proof that the eigenvalues of the corrected Smoluchowski operator become real for large enough friction.

In the concluding section we summarize our main conclusions. We also comment briefly on the connection to recent work by Gouyet(12) on the corrected Smoluchowski operator, and by Kuščer(13) on Onsager relations between transport coefficients appearing in the linearized Burnett equations.

Although the formalism developed in the paper is applicable to a broad class of linear mesoscopic equations, explicit calculations are presented only for the one-dimensional Klein–Kramers equation, which provides the simplest nontrivial example. This was done to enable us to concentrate on the conceptual issues involved. We intend to discuss some similar questions for the linearized Boltzmann equation in a subsequent paper.

2. THE ONSAGER–CASIMIR SYMMETRY OF THE KLEIN–KRAMERS EQUATION

The systems we shall deal with in this paper consist of noninteracting particles of mass m moving under the influence of a potential $\Phi(\mathbf{r})$. On the mesoscopic level the system is described by a distribution function $P(\mathbf{u}, \mathbf{r}, t)$ of particle velocities and positions, normalized to unity, which obeys a kinetic equation of the type

$$\frac{\partial P(\mathbf{u}, \mathbf{r}, t)}{\partial t} = -\mathbf{u}\cdot\frac{\partial P}{\partial \mathbf{r}} + \frac{1}{m}\frac{\partial \Phi}{\partial \mathbf{r}}\cdot\frac{\partial P}{\partial \mathbf{u}} + \gamma\mathscr{C}P \tag{2.1}$$

Here $\mathscr{C}$ is an operator acting on the velocity variables only. Moreover, we require that it satisfies the (extended) detailed balance condition$^{(14)}$ relative to a Maxwellian velocity distribution at a temperature $T=(k\beta)^{-1}$; the parameter γ is a bookkeeping parameter at this stage. In all explicit calculations we shall use the one-dimensional version of (2.1) and choose for $\mathscr{C}$ the expression

$$\mathscr{C} = \frac{1}{m\beta}\left(\frac{\partial^2}{\partial u^2} + \frac{\partial}{\partial u}u\right) \tag{2.2}$$

For this choice of $\mathscr{C}$, (2.1) describes an assembly of Brownian particles and is called the Klein–Kramers equation, while γ denotes the friction coefficient.

The distribution function $P(u, x, t)$ itself is not a suitable variable for our subsequent analysis, since it has no definite parity under the time-reversal transformation $u \to -u$. We therefore decompose it with respect to a complete set of functions $\phi_k(u)$ that do have definite parity:

$$P(u, x, t) = P_{\text{eq}}(u, x) + \sum_{k=0}^{\infty} a_k(x, t)\,\phi_k(u) \tag{2.3}$$

where $P_{\text{eq}}(u, x)$ is the normalized equilibrium distribution. It is convenient to choose for the $\phi_k(u)$ the eigenfunctions of (2.2) with eigenvalues $-k$. As was shown in Ref. 7, these are

$$\phi_k(u) = \frac{1}{k!\,(4\pi)^{1/2}(2m\beta)^{(k-1)/2}} H_k\left[\left(\frac{1}{2}m\beta\right)^{1/2} u\right] e^{-m\beta u^2/2} \tag{2.4a}$$

Their orthogonality properties are

$$\left(\frac{2\pi}{m\beta}\right)^{1/2} \int du\, e^{m\beta u^2/2}\, \phi_k(u)\, \phi_l(u) = \delta_{kl}\alpha_l; \qquad \alpha_l = [l!\,(m\beta)^l]^{-1} \tag{2.4b}$$

(the slightly awkward normalization is chosen to remain consistent with Ref. 9, from which we shall use several explicit results). The set of functions $\{a_k(x, t)\}$ will be our set of fundamental mesoscopic variables; they have time reversal parity $\eta_k = (-1)^k$. By expressing the first two terms in (2.1) in terms of the raising and lowering operators for the $\phi_k(u)$, one deduces from (2.1) the set of coupled evolution equations

$$\frac{\partial a_k(x, t)}{\partial t} = -\left[k\gamma a_k(x, t) + kD_x a_{k-1}(x, t) + \frac{1}{m\beta}\partial_x a_{k+1}(x, t)\right] \tag{2.5}$$

where we used the abbreviations

$$\partial_x \equiv \partial/\partial x, \qquad D_x \equiv \partial_x + \beta\Phi'(x) \tag{2.6}$$

The set (2.5) can be written symbolically as

$$\frac{\partial}{\partial t}\mathbf{a}(x, t) = \mathsf{M}\cdot\mathbf{a}(x, t) \tag{2.7}$$

where $\mathbf{a}$ is a vector consisting of functions and M is a matrix with elements that are operators with respect to x.

To bring (2.7) into the canonical form for testing Onsager symmetry, the variables $a_k(x, t)$ must be eliminated in favor of the thermodynamic force fields, i.e., contributions linear in the $a_l(x)$ to the functional derivatives of the thermodynamic potential with respect to the $a_k(x)$. Since $\mathscr{C}$ describes a coupling to a heat bath, the relevant thermodynamic potential is the free energy. The free energy functional is given by

$$\mathscr{F}[P(u, x, t)] = \frac{1}{\beta}\int du \int dx\, P(u, x, t) \ln[P(u, x, t)/P_{\mathrm{eq}}(u, x)] \tag{2.8}$$

If one now substitutes

$$P_{\mathrm{eq}}(u, x) = a_{00}(x)\,\phi_0(u) = N_0 \exp\left[-\frac{1}{2}m\beta u^2 - \beta\Phi(x)\right] \tag{2.9}$$

with N_0 a suitable normalization constant, inserts the expansion (2.3), and exploits the orthogonality relations (2.4), one obtains, up to terms quadratic in the $a_k(x, t)$,

$$\beta\mathscr{F}[P(u, x, t)] = \frac{1}{2}\sum_k \alpha_k \int dx\, a_{00}^{-1}(x)[a_k(x, t)]^2 \tag{2.10}$$

The thermodynamic force fields are therefore given by

$$f_k(x, t) = \beta^{-1}\alpha_k a_{00}^{-1}(x)\, a_k(x, t) \tag{2.11}$$

A straightforward analogy with the procedures outlined in Refs. 3 and 4 (cf. also Ref. 10) would require us to rewrite (2.7) as

$$\frac{\partial}{\partial t}\mathbf{a}(x, t) = \mathsf{M}\cdot\mathbf{a}(x, t) = \tilde{\mathsf{L}}\cdot\mathbf{f}(x, t) \tag{2.12}$$

The Onsager–Casimir symmetry requirement on $\tilde{\mathsf{L}}$ would then entail the condition

$$\tilde{L}_{kl} = (-1)^{k+l}\tilde{L}_{lk}^{\dagger} \tag{2.13}$$

for the matrix elements of $\tilde{\mathsf{L}}$, where the dagger denotes the Hermitian adjoint. The calculation of the $\tilde{L}_{kl}$ from (2.5), (2.11), and (2.12), and the subsequent verification of (2.13), is straightforward. However, one may save some labor by writing, instead of (2.12),

$$\mathsf{M}\cdot\mathbf{a}(x, t) = \mathsf{L}\cdot a_{00}(x)\,\mathbf{f}(x, t) \tag{2.14}$$

The requirement (2.13) is readily shown to be equivalent to

$$L_{kl} = (-1)^{k+l}L_{lk}^{+} \tag{2.15}$$

where the superscript plus sign denotes the Hermitian adjoint with respect to the weighted scalar product

$$\langle f, g\rangle = \int dx\, a_{00}^{-1}(x)\, f(x)\, g(x) \tag{2.16}$$

The matrix elements L_{kl} follow directly from (2.5):

$$L_{kl} = -\beta\left(\frac{\gamma k}{\alpha_k}\delta_{kl} + \frac{k}{\alpha_{k-1}}D_x\delta_{k,l+1} + \frac{1}{m\beta\alpha_{k+1}}\partial_x\delta_{k,l-1}\right) \tag{2.17}$$

from which one obtains, by substitution of (2.4),

$$L_{kl} = -\beta[\gamma k\, k!\,(m\beta)^k\delta_{kl} + k!\,(m\beta)^{k-1}D_x\delta_{k,l+1} + (k+1)!\,(m\beta)^k\,\partial_x\delta_{k,l-1}] \tag{2.18}$$

The validity of the Onsager–Casimir symmetry relations now immediately follows from the fact that D_x and $-\partial_x$ are a pair of Hermitian conjugates with respect to the scalar product (2.16).

The derivation given here for the Klein–Kramers equation may be generalized to a more general $\mathscr{C}$. If one uses the expansion (2.3), then the first term in (2.5) becomes slightly more complicated; it now contains a linear combination of $a_l(x, t)$ with constant coefficients. The properties (2.13) and (2.15) can still be proved; one has to rely on the fact that the extended detailed balance property of $\mathscr{C}$ is equivalent(14) to the required Hermiticity properties with respect to the scalar product

$$\langle f, g\rangle = \int du\, e^{m\beta u^2/2} f(u)\, g(u) \tag{2.19}$$

Finally, we would point out that the lowest order free energy functional (2.10) can also be obtained by expanding the expression

$$\beta\mathscr{F}[P(u, x, t)] = \int du \int dx\, P_{\text{eq}}^{-1}(u, x)[P(u, x, t)]^2 \tag{2.20}$$

known to be a Liapunov function for a general Fokker–Planck equation,(14) and hence also for the special case of the Klein–Kramers equation.

3. THE PROBLEM: VIOLATIONS OF ONSAGER SYMMETRY FOR THE CORRECTED SMOLUCHOWSKI EQUATION

In this section we consider the case where the friction γ is large, or, more precisely, where the potential varies slowly on the scale of the velocity persistence length $l = \gamma^{-1}(m\beta)^{-1/2}$. To avoid manifestly bad convergence of various expansions (which are in general merely asymptotic ones in any case), it is prudent to assume that the initial distribution $P(u, x, 0)$ is also smooth on that scale. Then, as is argued more fully in Refs. 7 and 8, the solution $P(u, x, t)$ will, on a time scale γ^{-1}, approach a normal (or Chapman–Enskog type) solution of the form

$$P^{[0]}(u, x, t) = [a_{00}(x) + c_0(x, t)]\, \phi_0(u) + \mathscr{O}(\gamma^{-1}) \tag{3.1}$$

The correction terms contain only $\phi_n(u)$ with $n > 0$; the coefficients of these $\phi_n(u)$ are completely determined by $c_0(x, t)$; they can be calculated via a perturbation algorithm as power series in γ^{-1}. As a solubility condition for this perturbation scheme there emerges the equation of motion that the function $c_0(x, t)$ must obey; we denote this equation by

$$\frac{\partial}{\partial t} c_0(x, t) = \mathscr{M} c_0(x, t) \tag{3.2}$$

Successive contributions to the operator $\mathcal{M}$ are found in successive orders in perturbation theory. [The function $c_0(x, t)$ differs from the one used in Ref. 7 by the term $a_{00}(x)$, but this is immaterial, since all terms in $\mathcal{M}$ annihilate $a_{00}(x)$].

To lowest order one obtains for $\mathcal{M}$ the Smoluchowski operator

$$\mathcal{M}^{(1)}=\frac{1}{m\beta\gamma}\,\partial_x(\partial_x+\beta\Phi')=\frac{1}{m\beta\gamma}\,\partial_x D_x \tag{3.3}$$

This operator is clearly Hermitian with respect to the scalar product (2.16). This Hermiticity is tantamount to Onsager symmetry if one defines the thermodynamic forces as functional derivatives of the coarse-grained free energy functional given by

$$\begin{aligned}\beta\mathscr{F}^{(0)}[c_0(x, t)]&=\int dx\,(c_0+a_{00})\ln\left(1+\frac{c_0}{a_{00}}\right)\\&\simeq\frac{1}{2}\int dx\,a_{00}^{-1}(x)[c_0(x, t)]^2\end{aligned} \tag{3.4}$$

where the second line is obtained by neglecting terms of third and higher order in c_0.

When terms up to order γ^{-5} are included in $\mathcal{M}$ one obtains^(7)

$$\begin{aligned}\mathcal{M}^{(5)}=\frac{1}{m\beta\gamma}\,\partial_x\Bigg\{1+\frac{1}{m\gamma^2}\,\Phi''+\frac{1}{(m\beta\gamma^2)^2}\Bigg[\frac{1}{2}\,\beta\Phi^{(iv)}+2\beta^2(\Phi'')^2\\-\frac{1}{2}\,\beta^2\Phi'\Phi'''+\frac{3}{2}\,\beta\Phi'''D_x\Bigg]\Bigg\}\,D_x+\mathcal{O}(\gamma^{-7})\end{aligned} \tag{3.5}$$

The last term clearly violates Hermiticity, as well as Onsager symmetry relative to the coarse-grained free energy (3.4). However, it was rather inconsistent to include higher corrections to $\mathcal{M}$, but not the contributions of the correction terms in the expression (3.1) for $P^{[0]}$ to the free energy functional. The explicit form of $P^{[0]}$ up to order γ^{-5} is given in Eq. (3.9) of Ref. 7. When one omits terms that do not contribute to $\mathscr{F}$ at order γ^{-4} (and corrects a misprint) one obtains

$$\begin{aligned}P^{[0]}(u, x, t)=[a_{00}(x)+c_0(x, t)]\,\phi_0(u)-\left(\frac{1}{\gamma}+\frac{1}{m\gamma^3}\,\Phi''\right)D_x c_0(x, t)\,\phi_1(u)\\+\frac{1}{\gamma^2}\,D_x^2 c_0(x, t)\,\phi_2(u)+\cdots\end{aligned} \tag{3.6}$$

By substitution into (2.10) and a few integrations by part, one obtains for the free energy up to order γ^{-4}

$$\beta\mathscr{F}[c_0(x,t)] = \frac{1}{2}\int dx\, a_{00}^{-1}(x)\, c_0(x,t)\, \mathscr{G} c_0(x,t) \tag{3.7}$$

where the operator $\mathscr{G}$ is given by

$$\mathscr{G} = 1 - \frac{1}{m\beta\gamma^2}\partial_x D_x + \frac{1}{(m\beta\gamma^2)^2}\left(\frac{1}{2}\partial_x^2 D_x^2 - 2\beta\partial_x \Phi'' D_x\right) \tag{3.8}$$

[we assume $\Phi(x)$ diverges fast enough at infinity so that boundary terms do not contribute]. As expected, $\mathscr{G}$ is Hermitian and positive definite with respect to the weighted scalar product (2.16).

The thermodynamic force field $f_0(x,t)$ conjugate to $c_0(x,t)$ is given by

$$f_0(x,t) = \beta^{-1} a_{00}^{-1}(x)\, \mathscr{G} c_0(x,t) \tag{3.9}$$

If one now recasts (3.2) into the form

$$\frac{\partial}{\partial t} c_0(x,t) = \mathscr{L} a_{00}(x)\, f_0(x,t) \tag{3.10}$$

in complete analogy with (2.14), and substitutes (3.9) as well as the expressions for $\mathscr{M}$ and $\mathscr{G}$, one obtains for the operator $\mathscr{L}$

$$\begin{aligned}\mathscr{L} = \frac{1}{m\gamma}\partial_x \Bigg[1 + \frac{1}{m\beta\gamma^2}\partial_x D_x + \frac{1}{(m\beta\gamma^2)^2}\bigg(\frac{1}{2}\partial_x^2 D_x^2 + \beta\partial_x \Phi'' D_x \\ + \frac{3}{2}\beta\Phi^{(iv)} - \frac{3}{2}\beta^2\Phi'\Phi''' + 2\beta\Phi''' D_x\bigg)\Bigg] D_x + \mathcal{O}(\gamma^{-6})\end{aligned} \tag{3.11}$$

The last term in large parentheses violates the Hermiticity condition equivalent to Onsager symmetry. The inclusion of correction terms in the free energy therefore does not remedy the lack of symmetry already apparent in the expression (3.5) for $\mathscr{M}$; it merely changes the coefficient of the troublesome term (and adds a few Hermitian terms as well).

Before proceeding toward a solution of the questions raised by this symmetry violation, we emphasize that the transition from the lowest order Chapman–Enskog result to the higher order approximations did not involve the introduction of additional variables or additional pairs of forces and fluxes. Thus our approach is fundamentally different in its philosophy from schemes known as "extended thermodynamics," which are widely criticized as unsystematic.(15) As soon as the Chapman–Enskog regime sets in, the $a_n(x, t)$ with $n > 0$ in (2.3) cease to be independent variables; they adiabatically adjust themselves to (or, in the parlance of Haken,⁽¹⁶⁾ are enslaved by) the macroscopic field $c_0(x, t)$.

4. A REMEDY: AN ALTERNATIVE DEFINITION OF THE THERMODYNAMIC FORCES

In complete analogy with the recipe given in Ref. 9, we shall now present a modification of the Onsager–Casimir symmetry relations that enables them to survive the adiabatic elimination of fast variables. For this purpose we take as the fundamental thermodynamic quantity, instead of the functional $\mathscr{F}$, the associated "thermodynamic Lagrangian" $\hat{\mathscr{F}}$, defined as the difference between the contributions of the odd variables to the quadratic approximation of $\mathscr{F}$ and those of the even variables. For our specific example one obtains instead of (2.10)

$$\beta\hat{\mathscr{F}}[P(u, x, t)] = -\frac{1}{2}\sum_k \alpha_k(-1)^k \int dx\, a_{00}^{-1}(x)[a_k(x, t)]^2 \tag{4.1}$$

Accordingly, we define the modified thermodynamic forces $\hat{f}_k(x, t)$ as the functional derivatives of $\hat{\mathscr{F}}$ with respect to the $a_k(x, t)$. For the Klein–Kramers system these are

$$\hat{f}_k(x, t) = (-1)^{k+1}\beta^{-1}\alpha_k a_{00}^{-1}(x)\, a_k(x, t) = (-1)^{k+1} f_k(x, t) \tag{4.2}$$

Next we define the new Onsager matrix operator $\hat{\mathsf{L}}$ via

$$\mathsf{M}\cdot\mathbf{a}(x, t) = \hat{\mathsf{L}}\cdot a_{00}(x)\,\hat{\mathbf{f}}(x, t) \tag{4.3}$$

A comparison with (2.14) shows that the matrix elements of $\hat{\mathsf{L}}$ and L are related, for our simple case, by

$$\hat{L}_{kl} = (-1)^{l+1} L_{kl} \tag{4.4}$$

Using (2.15), one obtains as the modified Onsager–Casimir conditions

$$\hat{L}_{kl} = (-1)^{l+1} L_{kl} = (-1)^{k+1} L_{lk}^{+} = \hat{L}_{lk}^{+} \tag{4.5}$$

Thus, the modified Onsager matrix operator is always Hermitian, even when some of the variables are odd under time reversal. This conclusion, unlike (4.1)–(4.4), does not depend on the "diagonal" form (2.10) of the free energy, as can be seen by retracing the analogous derivation in Ref. 9.

By replacing the $a_k(x, t)$ in (4.1) by the coefficient functions in the Chapman–Enskog solution (3.6) one obtains for the thermodynamic Lagrangian of this normal solution

$$\beta\hat{\mathcal{F}}[c_0(x, t)] = \frac{1}{2}\int dx\, a_{00}^{-1}(x)\, c_0(x, t)\, \hat{\mathcal{G}} c_0(x, t) \tag{4.6}$$

with, up to fourth order in γ^{-1},

$$\hat{\mathcal{G}} = -\left[1 + \frac{1}{m\beta\gamma^2}\partial_x D_x + \frac{1}{(m\beta\gamma^2)^2}\left(\frac{1}{2}\partial_x^2 D_x^2 + 2\beta\partial_x \Phi'' D_x\right)\right] \tag{4.7}$$

If one now writes the equation of motion (3.2) in the form analogous to (3.10),

$$\frac{\partial}{\partial t} c_0(x, t) = \mathcal{M} c_0(x, t) = \beta^{-1}\hat{\mathcal{L}}\hat{\mathcal{G}} c_0(x, t) = \hat{\mathcal{L}} a_{00}(x)\, \hat{f}_0(x, t) \tag{4.8}$$

and substitutes the approximations (3.5) and (4.7) for $\mathcal{M}$ and $\hat{\mathcal{G}}$, one obtains

$$\hat{\mathcal{L}} = -\frac{1}{m\gamma}\partial_x\left\{1 - \frac{1}{m\beta\gamma^2}(\partial_x D_x - 2\beta\Phi'') + \frac{1}{(m\beta\gamma^2)^2}\left[\frac{1}{2}\partial_x^2 D_x^2 - 5\beta\partial_x\Phi'' D_x \right.\right.$$
$$\left.\left. - \frac{5}{2}\beta\Phi^{(iv)} + 6\beta^2(\Phi'')^2 + \frac{5}{2}\beta^2\Phi'\Phi'''\right]\right\} D_x \tag{4.9}$$

Thus, $\hat{\mathcal{L}}$, unlike $\mathcal{L}$, is Hermitian with respect to (2.16).

The operator $\hat{\mathcal{G}}$ that relates the modified thermodynamic force field $\hat{f}_0(x, t)$ to the macroscopic field $c_0(x, t)$ also plays an important role in the analysis of the spectral properties of the evolution operator $\mathcal{M}$. Suppose $c_\lambda(x)$ is an eigenfunction of $\mathcal{M}$ with eigenvalue m_λ:

$$\mathcal{M} c_\lambda(x) = \beta^{-1}\hat{\mathcal{L}}\hat{\mathcal{G}} c_\lambda(x) = m_\lambda c_\lambda(x) \tag{4.10}$$

By a slight adaptation of the proof in Ref. 10 we shall now show that

$$\hat{f}_\lambda(x) = a_{00}^{-1}(x)\, \hat{\mathcal{G}} c_\lambda(x) \tag{4.11}$$

is a left eigenfunction of $\mathcal{M}$ (i.e., an eigenfunction of $\mathcal{M}^\dagger$) with the same eigenvalue. From the relations

$$\partial_x a_{00} f = a_{00}(\partial_x - \beta\Phi') f = -a_{00} D_x^\dagger f; \qquad D_x a_{00} f = a_{00}\partial_x f = -a_{00}\partial_x^\dagger f \tag{4.12}$$

which follow immediately from $a_{00}(x) \sim \exp[-\beta\Phi(x)]$, one readily derives an interesting connection between Hermiticity properties relative to weighted and unweighted scalar products. For any operator $\mathscr{A}$ with $\mathscr{A} = \mathscr{A}^+$ one finds (by substituting $f = a_{00}^{-1} g$)

$$\mathscr{A}^\dagger a_{00}^{-1}(x)\, g(x) = a_{00}^{-1}(x)\, \mathscr{A} g(x) \tag{4.13}$$

Since $\hat{\mathscr{L}} = \hat{\mathscr{L}}^+$ and $\hat{\mathscr{G}} = \hat{\mathscr{G}}^+$, one therefore has

$$\mathscr{M}^\dagger a_{00}^{-1} \hat{\mathscr{G}} c_\lambda = \beta^{-1} \hat{\mathscr{G}}^\dagger \hat{\mathscr{L}}^\dagger a_{00}^{-1} \hat{\mathscr{G}} c_\lambda = \beta^{-1} a_{00}^{-1} \hat{\mathscr{G}} \hat{\mathscr{L}} \hat{\mathscr{G}} c_\lambda = m_\lambda a_{00}^{-1} \hat{\mathscr{G}} c_\lambda \tag{4.14}$$

or, inserting the definition (4.11),

$$\mathscr{M}^\dagger \hat{f}_\lambda(x) = m_\lambda \hat{f}_\lambda(x) \tag{4.15}$$

which proves the above assertion. The connection between c_λ and $\hat{f}_\lambda$ leads to the orthogonality relation

$$\int dx\, c_\lambda(x)\, \hat{f}_\mu(x) = \int dx\, a_{00}^{-1}(x)\, c_\lambda(x)\, \hat{\mathscr{G}} c_\mu(x) = 0 \qquad (m_\lambda \neq m_\mu) \tag{4.16}$$

for the eigenfunctions c_λ of the corrected Smoluchowski operator $\mathscr{M}$.

The operator $\hat{\mathscr{G}}$ in (4.16) is Hermitian with respect to the weighted scalar product, and approaches $-\mathscr{J}$ for large γ. This implies that the operator $(-\hat{\mathscr{G}})^{1/2}$ can be constructed at least as a formal power series in γ^{-1}. We now consider the operator

$$\hat{\mathscr{Q}} \equiv -\beta^{-1} a_{00}^{-1/2} (-\hat{\mathscr{G}})^{1/2} \hat{\mathscr{L}} (-\hat{\mathscr{G}})^{1/2} a_{00}^{1/2} \tag{4.17}$$

One readily checks that

$$\hat{\mathscr{Q}} a_{00}^{-1/2} (-\hat{\mathscr{G}})^{1/2} c_\lambda = a_{00}^{-1/2} (-\hat{\mathscr{G}})^{1/2} \mathscr{M} c_\lambda = m_\lambda a_{00}^{-1/2} (-\hat{\mathscr{G}})^{1/2} c_\lambda \tag{4.18}$$

Hence, $\hat{\mathscr{Q}}$ and $\mathscr{M}$ have the same eigenvalues. On the other hand, $\hat{\mathscr{Q}}$ has the form $a_{00}^{-1/2} \mathscr{A} a_{00}^{1/2}$ with $\mathscr{A} = \mathscr{A}^+$. This implies that $\hat{\mathscr{Q}}$ is Hermitian: from (4.13) one deduces

$$a_{00}^{-1/2} \mathscr{A} a_{00}^{1/2} = a_{00}^{-1/2} \mathscr{A} a_{00} a_{00}^{-1/2} = a_{00}^{1/2} \mathscr{A}^\dagger a_{00}^{-1/2} = (a_{00}^{-1/2} \mathscr{A} a_{00}^{1/2})^\dagger \tag{4.19}$$

Thus, all eigenvalues of $\mathscr{M}$ are also eigenvalues of a Hermitian operator, hence they must all be real (and, in view of the existence of a Liapunov function, all negative but for the simple eigenvalue zero).

This conclusion is, however, far from rigorous. Our expressions for $\mathscr{M}$, $\hat{\mathscr{G}}$, and $\hat{\mathscr{L}}$ are purely formal power series in γ^{-1}, and not much is known about their convergence properties (probably the series are asymptotic ones, except in very simple cases). On the other hand, the eigenvalues and eigenfunctions of the Smoluchowski operator $\mathscr{M}^{(1)}$, given by (3.3), are known to be real, since $\mathscr{M}^{(1)}$ can be transformed into a Schrödinger operator.(17) Since all correction terms in $\mathscr{M}$ are real operators, this implies that all terms in the perturbation expansion for the eigenvalues and eigenfunctions of $\mathscr{M}$, with $\mathscr{M}-\mathscr{M}^{(1)}$ taken as the perturbation, are real as well. Also, analytical(7) and numerical(18) calculations of the eigenvalues of the Klein–Kramers equation for specific potentials as functions of γ^{-1} show that each of them stays real for a range of values of γ^{-1}, until they intersect another eigenvalue at a branch point, from which then typically two complex eigenvalues emerge. The analogy with the results in Ref. 11 leads one to expect that at such a branch point the expectation value of the thermodynamic Lagrangian in the eigenfunctions involved goes to zero; this implies that one is at or beyond the radius of convergence of the power series expression for $(-\hat{\mathscr{G}})^{1/2}c_\lambda$.

5. CONCLUDING REMARKS

The deviations from Onsager–Casimir symmetry considered in this paper, especially in Section 3, are most probably too small to be of any practical importance. In addition, if a discrepancy were to be measured, it would be very difficult to ascertain whether it corresponds to correction terms arising during the transition from a microscopic to a mesoscopic description or from the corrections arising during the transition from the mesoscopic to the macroscopic level, which were determined in this paper.[3] However, the Onsager–Casimir relations have an additional importance: they provide insight into the spectral properties of macroscopic (and mesoscopic) evolution operators, and they can serve as useful checks on practical calculations. It is gratifying that the modified Onsager relations introduced in Section 4 perform these secondary functions just as well as the original Onsager–Casimir relations.

The modified definition of the thermodynamic forces has some advantages in addition to enabling the Onsager–Casimir relations to survive the adiabatic elimination of some of the variables. The most important one is that the time evolution of the new thermodynamic force fields is governed by the Hermitian adjoint of the evolution operator for the fundamental variables:

$$d\mathbf{a}/dt = \mathsf{M}\cdot\mathbf{a} \Leftrightarrow d\hat{\mathbf{f}}/dt = \mathsf{M}^{\dagger}\cdot\hat{\mathbf{f}} \tag{5.1}$$

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[3] A calculation of correction terms arising from the first transition could be carried out for the case of a Brownian particle in the framework of the theory given in Ref. 19.

where M may be a matrix, an operator, or an operator matrix. A proof is readily constructed by adaptation of the one in Ref. 10 or the one in this paper leading to (4.15).

A related advantage of the modified definition is caused by the diagonality of the mesoscopic functional $\hat{\mathscr{F}}[P]$ with respect to the spectral decomposition of M (see Ref. 10). Thus, for a mesoscopic solution

$$\mathbf{a}(x, t) = \mathbf{a}_{\mathrm{CE}}(x, t) + \mathbf{a}_t(x, t) \tag{5.2}$$

with a Chapman–Enskog component $\mathbf{a}_{\mathrm{CE}}$ and a fast transient $\mathbf{a}_t$, there is a corresponding decomposition of the modified thermodynamic force

$$\hat{\mathbf{f}}(x, t) = \hat{\mathbf{f}}_{\mathrm{CE}}(x, t) + \hat{\mathbf{f}}_t(x, t) \tag{5.3}$$

with a slow part $\hat{\mathbf{f}}_{\mathrm{CE}}$ depending only on $\mathbf{a}_{\mathrm{CE}}$ and a fast part $\hat{\mathbf{f}}_t$ depending only on $\mathbf{a}_t$. This means that the two parts of $\mathbf{a}$ obey separate equations of the typical Onsager form, in particular

$$\frac{\partial}{\partial t} \mathbf{a}_{\mathrm{CE}}(x, t) = \hat{\mathsf{L}} a_{00}(x)\, \hat{\mathbf{f}}_{\mathrm{CE}}(x, t) \tag{5.4}$$

This is a closed equation for $\mathbf{a}_{\mathrm{CE}}$, from which the Hermiticity of the reduced Onsager operator $\hat{\mathscr{L}}$ of Section 4 can be proved using the techniques of Ref. 9. On the other hand, the functional $\mathscr{F}[P]$ is not diagonal in the above sense. In a decomposition of $\mathbf{f}$ analogous to (5.3) the slow component of $\mathbf{f}$ also depends on $\mathbf{a}_t$, and the fast one on $\mathbf{a}_{\mathrm{CE}}$. The mesoscopic operator L, unlike $\hat{\mathsf{L}}$, couples Chapman–Enskog and transient parts of the solution.

A final, rather minor, advantage of the redefinition of the thermodynamic forces is that it allows one to extend the original Onsager formulation of the symmetry relations (for even variables only) to the Casimir case, where some of the variables are odd, without introducing extra sign factors.

The spectral equivalence proved in Section 4 between the macroscopic evolution operator $\mathscr{M}$ and the Hermitian operators $\hat{\mathscr{Q}}$ answers a question raised in a recent paper by Gouyet.(12) This author succeeded in transforming low-order approximations to $\mathscr{M}$, and analogues for the faster decaying solutions of the Klein–Kramers equation, into Hermitian operators via a transformation of the type

$$c_0(x, t) \to g(x)\, c_0(x, t), \qquad \mathscr{M} \to g \mathscr{M} g^{-1} \tag{5.5}$$

This transformation is clearly not general enough to perform its assigned task up to arbitrary order in γ^{-1}. When applied to the operator $\mathscr{M}^{(5)}$ in (3.5) it can never change the order of the highest differential operator (nor its coefficient) and thus remove the differential operator of third order, which precludes Hermiticity. For such a task one needs to include a differential operator in the transformation of $c_0(x, t)$. On the other hand, our procedure can be applied equally well to the reduced evolution operators for more rapidly decaying solutions of the Klein–Kramers equation. The essential requirement is that all variables in the reduced description have the same time reversal parity, to allow the quantity corresponding to $(\pm\hat{\mathscr{G}})^{1/2}$ to be well-defined.

For equations such as the linearized Boltzmann equation one has more than one single hydrodynamic field $c_0(x, t)$. Thus, the operator $\mathscr{M}$ becomes an operator matrix. Successive approximations to it represent the Euler, Navier–Stokes, Burnett, and super-Burnett equations, and Onsager-type relations derived by the methods outlined in this paper express themselves as constraints on the form of these equations and on the coefficients appearing in them. This to us appears to be the "royal road" toward deriving Onsager relations (or deviations from them) for Burnett and super-Burnett coefficients. Another approach might be to expand the hydrodynamic fields in terms of a complete set of functions of x (or $\mathbf{r}$) and to adopt the expansion coefficients as macroscopic variables for the system. This is the procedure that leads to the conventional Onsager relations for continuous systems where all hydrodynamic fields are linear functions of the space variables, and it appears to be the approach chosen by Kuščer in a recent paper.(13) He restricts himself to fields that depend polynomially on the space coordinates; in that case the coefficients of the polynomials are related rather simply to the values of the expansion coefficients in the analog of (3.6) in a given point in space, which were chosen by Kuščer as the fundamental fluxes. It is not clear, however, whether such a relation is generally valid, and, perhaps more importantly, under which conditions a truncation of the set of equations for the expansion coefficients of the hydrodynamic fields can be justified. In this connection we wish to stress once more that the number of independent variables is fixed by the level of description chosen for the system. It may be further restricted by the boundary conditions imposed (symmetry, restriction to stationary solutions of the hydrodynamic equations). It does not depend on the order up to which the Chapman–Enskog perturbation scheme is carried through.

In view of the partial integrations involved in the definition of $\mathscr{G}$ and $\hat{\mathscr{G}}$ and the concomitant neglect of boundary terms in the free energy, our treatment needs some extension before it can be applied to open systems, in particular when they are not large compared to the velocity persistence length (in the kinetic theory of gases the mean free path, respectively). In any case, in such systems the Chapman–Enskog approximation is expected to break down in the boundary layers(20) and a more detailed treatment is called for.

Finally, we stress once more that our treatment, though for ease of exposition restricted mainly to the Klein–Kramers case, should be extendable to any system described on the mesoscopic level by a linear equation satisfying an extended detailed balance condition. After all, it is to a large extent merely a transcription of the treatment developed in Ref. 9 for systems with a finite number of thermodynamic coordinates. Once the appropriate thermodynamic variables for each level of description of a physical system are identified, the required adaptation of the formalism becomes rather straightforward.

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