

## **Onsager–Casimir Symmetry Properties of the Burnett Equations**

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We demonstrate the approximate nature of the Onsager–Casimir relations for the example of the linearized Burnett equations for a dilute gas. For any discussion of Onsager relations the choice of a correct set of thermodynamic forces and fluxes is of course crucial. By retracing the Chapman–Enskog procedure, we show that the usual expressions for the thermodynamic forces require modifications at the Burnett level. However, inclusion of these terms does not remedy the violation of Onsager symmetry first noticed by McLennan. A modified version of the Onsager symmetry that involves thermodynamic forces derived from an entropy Lagrangian rather than from the entropy itself does remain valid on the Burnett level. Throughout, we allow for the presence of an external potential; the Burnett equations including potential terms are derived in an appendix for a set of variables particularly suited for our discussion. We stress that in discussing Onsager relations one should use the full thermodynamic fluxes rather than their dissipative parts only, in spite of the fact that only the latter contribute to the entropy production.

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**KEY WORDS:** Onsager–Casimir relations; adiabatic elimination; Chapman–Enskog method; Boltzmann equation; Burnett equations; thermodynamic forces.

### **1. INTRODUCTION AND SURVEY**

The Onsager–Casimir reciprocity relations,<sup>(1–4)</sup> which are of fundamental importance in linear irreversible thermodynamics, are only approximately valid. This fact has been known for some time, but not much attention has been paid to it, probably since the deviations from Onsager symmetry are seldom of much practical significance. We feel that these deviations nevertheless deserve some attention, if only because of the central role played by the Onsager relations in the theoretical framework of statistical

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physics. The violations appear naturally in the course of a systematic analysis of the relation between the various levels of description (microscopic, mesoscopic, and macroscopic) that are appropriate for phenomena occurring in a given system on different time scales. Such an analysis also points the way toward a redefinition of the thermodynamic forces that restores full Onsager–Casimir symmetry.

The first indication of a violation of Onsager symmetry appeared in a paper by McLennan,<sup>(5)</sup> who showed by inspection that Onsager symmetry is violated by the Burnett corrections to the Navier–Stokes equations. As we shall see, McLennan’s case against the Onsager relations is not air-tight, since his expression for the thermodynamic forces neglects corrections to the entropy density of the same order as the Burnett corrections themselves. However, his conclusions remain valid when the appropriate correction terms are included. Moreover, McLennan correctly identified the fundamental cause of the symmetry violations, the “initial slip”<sup>(6,9,10)</sup> that occurs when one connects the solutions of the hydrodynamic equations, which are valid only after some “aging” period, to the actual initial values of the associated microscopic expressions.

Geigenmüller *et al.*<sup>(7)</sup> showed that violations of Onsager–Casimir symmetry occur quite generally when one carries out a systematic adiabatic elimination of fast variables from a system of relaxation equations that itself obeys the symmetry. The effect is again related to initial slip effects. In Ref. 7 it is also shown how the symmetry can be salvaged by a redefinition of the thermodynamic forces. The treatment of Ref. 7 is restricted to finite systems of relaxation equations. It was extended to continuous systems in a previous paper,<sup>(8)</sup> further designated by I, to which we refer for a somewhat fuller discussion. The formalism developed in I was applied there to the corrected Smoluchowski equation for the diffusion of Brownian particles in configuration space in the presence of an external potential. This equation can be derived from the Klein–Kramers equation for the diffusion of the Brownian particles in phase space by means of an adiabatic elimination of the velocity variable via the Chapman–Enskog procedure.<sup>(9,10)</sup> In the present paper we apply the formalism of Ref. 7 to the linearized Burnett equations, which can similarly be derived from the linearized Boltzmann equation.

Deviations from Onsager symmetry occur only when higher order corrections in the time scale ratio are included in an adiabatic elimination scheme. Hence, the linearized Boltzmann equation, which involves no such corrections, is expected to exhibit full Onsager symmetry when the usual conditions for its validity are satisfied. First of all, the microscopic equations should be time-reversal-invariant. This implies the absence of external magnetic fields or Coriolis forces, and it manifests itself in a

detailed balance property of the collision operator. Second, the stationary state around which one linearizes should itself be time-reversal-invariant (no macroscopic flow). In Section 2 we show how these conditions lead to the Onsager symmetry of the evolution equations for the expansion coefficients of the one-particle phase space distribution function with respect to a suitably chosen system of orthogonal functions of the velocity. It is important that the thermodynamic fluxes occurring in these mesoscopic Onsager relations are derived from the full evolution equations; they therefore contain both dissipative and nondissipative contributions. Our mesoscopic Onsager relations are closely related to, but not identical with, the Onsager relations recently proposed by Kuščer<sup>(11)</sup> for the hydrodynamic regime.

In Section 3 we consider the hydrodynamic equations, evaluated up to Burnett order. These can be derived from the Boltzmann equation using the Chapman–Enskog algorithm. We show the violation of Onsager symmetry already noticed by McLennan<sup>(5)</sup>; our treatment includes the effects of an external potential and a refined definition of the thermodynamic forces. The Chapman–Enskog solution is discussed more fully in the Appendix. Our treatment there largely follows the review by Dorfman and van Beijeren,<sup>(12)</sup> but it includes the effects of an external potential and the Chapman–Enskog expansion of the entropy functional, which is needed to obtain the correct expression for the thermodynamic forces.

In Section 4 we show how full Onsager–Casimir symmetry can be restored by modifying the definition of the thermodynamic forces. The modified forces are the functional derivatives with respect to the hydrodynamic fields of the “entropy Lagrangian,” i.e., the difference between the contributions to the entropy from the odd and those from the even part of the phase distribution function. We also comment on the use of these modified Onsager relations for establishing an upper bound for the number of propagating modes in a homogeneous system. These so called Lekkerkerker–Laidlaw relations<sup>(13,14)</sup> were already discussed in the present context in Ref. 5; they are closely related to generalized orthogonality relations for the eigenfunctions of the hydrodynamic evolution operator, noticed by Felderhof and Titulaer<sup>(15)</sup> and more fully discussed in the present context in I.

The final section contains some concluding remarks and some further comments on the relation of our treatment to that in Refs. 11 and 5. We briefly comment on the use that can be made of the modified Onsager relations for restricting phenomenologically derived equations of motion, and on the complications caused by kinetic boundary layers.

## 2. THE MESOSCOPIC ONSAGER-CASIMIR RELATIONS

The system considered in this paper is a dilute gas of structureless particles with mass  $m$  in a potential  $\Phi(\mathbf{r})$ . The gas should not be too far away from an equilibrium state described by the distribution function

$$P_{\text{eq}}(\mathbf{v}, \mathbf{r}) = \phi_0(\mathbf{v}) n_{\text{eq}}(\mathbf{r}) \quad (2.1)$$

where  $\phi_0(\mathbf{v})$  is the normalized Maxwell distribution at a temperature  $T_0 = (k\beta)^{-1}$  and  $n_{\text{eq}}(\mathbf{r})$  is given by

$$n_{\text{eq}}(\mathbf{r}) = N_0 \exp[-\beta\Phi(\mathbf{r})] \quad (2.2)$$

with  $N_0$  a normalization constant determined by the total number of particles. We shall assume that the one-particle distribution function  $P(\mathbf{v}, \mathbf{r}, t)$  of the gas obeys the linearized Boltzmann equation

$$\begin{aligned} \frac{\partial}{\partial t} P(\mathbf{v}, \mathbf{r}, t) &= (\mathcal{S} + \mathcal{R}) P(\mathbf{v}, \mathbf{r}, t) \\ &= \left( -\mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} + \frac{1}{m} \frac{\partial \Phi}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{v}} \right) P + \mathcal{R}P \end{aligned} \quad (2.3)$$

where  $\mathcal{R}$  is the linearized collision operator; it has the form  $n_{\text{eq}}(\mathbf{r}) \mathcal{R}_0$ , where  $\mathcal{R}_0$  acts only on  $\mathbf{v}$ . Equation (2.3) is a good approximation when  $P$  is sufficiently close to  $P_{\text{eq}}$ , and when both  $P$  and  $\Phi$  are sufficiently smooth (in  $\mathbf{r}$  on the scale of a mean free path). When the microscopic equations governing the collisions are invariant under time reversal,  $\mathcal{R}$  obeys the detailed balance condition, which is equivalent to Hermiticity with respect to the scalar product

$$\langle f, g \rangle_v = \int d\mathbf{v} f(\mathbf{v}) g(\mathbf{v}) \phi_0^{-1}(\mathbf{v}) \quad (2.4)$$

Moreover, it preserves the tensorial character of any function of  $\mathbf{v}$ , and in particular the parity with respect to time reversal (i.e., a change in the sign of  $\mathbf{v}$ ). The streaming operator  $\mathcal{S}$  in (2.3) reverses the parity and is anti-Hermitian with respect to

$$\langle P, Q \rangle_{r,v} = \int d\mathbf{v} \int d\mathbf{r} P(\mathbf{v}, \mathbf{r}) Q(\mathbf{v}, \mathbf{r}) P_{\text{eq}}^{-1}(\mathbf{v}, \mathbf{r}) \quad (2.5)$$

In order to discuss the Onsager symmetry properties of (2.3), we first have to choose a set of basic (in our case mesoscopic) variables with well-defined parity. The information contained in these variables should be

equivalent to that contained in  $P(\mathbf{v}, \mathbf{r}, t)$ . Once the basic variables are chosen, the thermodynamic fluxes and forces are also fixed<sup>(3)</sup>; they are the time derivatives of the variables and the functional derivatives of the entropy functional with respect to these variables, respectively. We choose as our variables the expansion coefficients  $c_k(\mathbf{r}, t)$  defined by

$$P(\mathbf{v}, \mathbf{r}, t) = P_{\text{eq}}(\mathbf{v}, \mathbf{r}) + \sum_{i=0}^{\infty} c_i(\mathbf{r}, t) \phi_i(\mathbf{v}) \quad (2.6)$$

where the  $\phi_k(\mathbf{v})$  are a set of functions of definite parity that are complete and orthogonal with respect to (2.4):

$$\langle \phi_i, \phi_j \rangle_v = \alpha_i \delta_{ij} \quad (2.7)$$

The first of these functions should be the Maxwellian  $\phi_0(\mathbf{v})$  and it is convenient to take the next four to be eigenfunctions of  $\mathcal{R}$  with eigenvalue zero; for later convenience we choose

$$\phi_{1,2,3}(\mathbf{v}) = m\beta v_{1,2,3} \phi_0(\mathbf{v}); \quad \phi_4(\mathbf{v}) = \frac{2}{3} \beta^2 \left( \frac{mv^2}{2} - \frac{3}{2\beta} \right) \phi_0(\mathbf{v}) \quad (2.8)$$

If one inserts the expansion (2.6) into the entropy functional

$$S[P(\mathbf{v}, \mathbf{r}, t)] = -k \int d\mathbf{r} \int d\mathbf{v} P(\mathbf{v}, \mathbf{r}, t) \ln[P(\mathbf{v}, \mathbf{r}, t)/P_{\text{eq}}(\mathbf{v}, \mathbf{r})] \quad (2.9)$$

one obtains, up to terms quadratic in the  $c_k$ ,

$$S^{[2]}[P] = -\frac{1}{2} k \sum_i \alpha_i \int d\mathbf{r} n_{\text{eq}}^{-1}(\mathbf{r}) [c_i(\mathbf{r}, t)]^2 \quad (2.10)$$

provided the integral over  $c_0(\mathbf{r}, t)$  vanishes (which means that  $P$  and  $P_{\text{eq}}$  contain the same number of particles). Hence the thermodynamic forces are given by

$$f_i(\mathbf{r}, t) = -\frac{\delta S^{[2]}[P]}{\delta c_i(\mathbf{r}, t)} = k\alpha_i n_{\text{eq}}^{-1}(\mathbf{r}) c_i(\mathbf{r}, t) \quad (2.11)$$

A decomposition of (2.3) with respect to the  $\phi_i(\mathbf{v})$  leads to a system of coupled evolution equations of the form

$$\frac{\partial}{\partial t} c_i(\mathbf{r}, t) = \sum_j \mathcal{M}_{ij} c_j(\mathbf{r}, t) \quad (2.12)$$

where the  $\mathcal{M}_{ij}$  are operators with respect to  $\mathbf{r}$ , due to the contributions originating in  $\mathcal{S}$ . Using (2.11), this is easily brought into the canonical Onsager form

$$\frac{\partial}{\partial t} c_i(\mathbf{r}, t) = \sum_j \tilde{\mathcal{L}}_{ij} f_j(\mathbf{r}, t) \quad (2.13)$$

In complete analogy with I, one derives from the Hermiticity properties of  $\mathcal{R}$  and  $\mathcal{S}$  the Onsager–Casimir relations

$$\tilde{\mathcal{L}}_{ij} = \eta_i \eta_j \tilde{\mathcal{L}}_{ji}^\dagger \quad (2.14)$$

where the dagger denotes Hermitian conjugation and the  $\eta_i$  are the parities of the functions  $\phi_i(\mathbf{v})$ . An alternative form, already introduced in I, is obtained by writing instead of (2.13)

$$\frac{\partial}{\partial t} c_i(\mathbf{r}, t) = \sum_j \mathcal{L}_{ij} n_{\text{eq}}(\mathbf{r}) f_j(\mathbf{r}, t) \quad (2.15)$$

The  $\mathcal{L}_{ij}$  then obey the relations

$$\mathcal{L}_{ij} = \eta_i \eta_j \mathcal{L}_{ji}^\dagger \quad (2.16)$$

where the superscript  $+$  denotes Hermitian conjugation with respect to the scalar product

$$\langle f, g \rangle_r = \int d\mathbf{r} n_{\text{eq}}^{-1}(\mathbf{r}) f(\mathbf{r}) g(\mathbf{r}) \quad (2.17)$$

It may be worth emphasizing that the thermodynamic fluxes, which can be written as

$$J_i(\mathbf{r}, t) \equiv \frac{\partial}{\partial t} c_i(\mathbf{r}, t) = \alpha_i^{-1} \langle \phi_i, (\mathcal{S} + \mathcal{R}) P(\mathbf{v}, \mathbf{r}, t) \rangle_v \quad (2.18)$$

can be decomposed naturally into a conservative part  $J_i^c$  containing the contributions from  $\mathcal{S}$ , and a dissipative part  $J_i^d$  containing the contributions from  $\mathcal{R}$ . Only the latter part contributes to the entropy production, which for the linearized Boltzmann equation is given by<sup>(4)</sup>

$$\sigma[P] = -k \int d\mathbf{r} \int d\mathbf{v} \mathcal{R} P(\mathbf{v}, \mathbf{r}, t) \ln[P(\mathbf{v}, \mathbf{r}, t)/P_{\text{eq}}(\mathbf{v}, \mathbf{r})] \quad (2.19)$$

An expansion in terms of the  $\phi_i$  in which only terms up to second in the  $c_i(\mathbf{r}, t)$  are retained gives

$$\begin{aligned} \sigma^{[2]}[P] &= k \sum_i \alpha_i \int d\mathbf{r} J_i^d(\mathbf{r}, t) c_i(\mathbf{r}, t) n_{\text{eq}}^{-1}(\mathbf{r}) \\ &= \sum_i \int d\mathbf{r} J_i^d(\mathbf{r}, t) f_i(\mathbf{r}, t) \end{aligned} \tag{2.20}$$

where due to the choice (2.8) only terms with  $i > 4$  contribute. From (2.18) and (2.11) one finds the relation

$$J_i^d(\mathbf{r}, t) = \sum_j \alpha_i^{-1} \langle \phi_i, \mathcal{R} \phi_j \rangle_v \alpha_j^{-1} n_{\text{eq}}(\mathbf{r}) f_j(\mathbf{r}, t) \tag{2.21}$$

In view of the Hermiticity of  $\mathcal{R}$  with respect to (2.4), the matrix connecting the  $J_i^d$  with the  $f_j$  is clearly symmetric. Since  $\mathcal{R}$ , moreover, connects only  $\phi_i$  and  $\phi_j$  with the same parity, this symmetry property is formally analogous to Onsager symmetry. It is highly misleading, however, to call it Onsager symmetry, as is clearly seen when one considers the influence of a magnetic field or of Coriolis forces. These add terms to  $\mathcal{S}$  that destroy its anti-Hermiticity, and hence the validity of the Onsager relations (2.14) or (2.16). However,  $\mathcal{R}$  is in general not affected (certainly not for hard spheres), so the matrix in (2.21) will in general stay symmetric. We return to this question in Section 5 in connection with a discussion of the work in Ref. 11.

### 3. SYMMETRY VIOLATION FOR THE BURNETT EQUATIONS

After an aging period of the order of a few mean free times, any sufficiently smooth solution of the linearized Boltzmann equation approaches a normal or Chapman–Enskog-type solution. In this so-called hydrodynamic stage the  $c_i(\mathbf{r}, t)$  with  $i > 4$  are linear functionals of the  $c_i(\mathbf{r}, t)$  with  $i \leq 4$ . The latter are called hydrodynamic fields; they will be denoted collectively by  $\mathbf{c}(\mathbf{r}, t)$ .<sup>2</sup> Moreover, the  $\mathbf{c}(\mathbf{r}, t)$  obey a closed set of linear evolution equations of the type

$$\frac{\partial}{\partial t} \mathbf{c}(\mathbf{r}, t) = \mathbf{M} \cdot \mathbf{c}(\mathbf{r}, t) \tag{3.1}$$

With the choice (2.8) for the relevant  $\phi_i(\mathbf{v})$  the field  $c_0(\mathbf{r}, t)$  is the excess particle density, the vector field  $\mathbf{c}(\mathbf{r}, t)$  with components  $c_{1,2,3}(\mathbf{r}, t)$  is the current density, and the field  $c_4(\mathbf{r}, t)$  is the excess kinetic energy density.

<sup>2</sup> In the remainder of this paper we use boldface and boldface sans serif type for three-dimensional vectors and tensors; five-dimensional vectors and tensors will be denoted by lowercase and capital lightface sans serif type, respectively.

The connection with the usual hydrodynamic fields  $\delta n$ ,  $\mathbf{u}$ , and  $\delta T$  is given by

$$\begin{aligned} c_0(\mathbf{r}, t) &= \delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - n_{\text{eq}}(\mathbf{r}) \\ \mathbf{c}(\mathbf{r}, t) &= n(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) \\ c_4(\mathbf{r}, t) &= \frac{3}{2}kn(\mathbf{r}, t) \delta T(\mathbf{r}, t) = \frac{3}{2}kn(\mathbf{r}, t)[T(\mathbf{r}, t) - T_0] \end{aligned} \quad (3.2)$$

We shall not make this change of variables, since the  $\mathbf{c}(\mathbf{r}, t)$  have a particularly simple relation to the associated thermodynamic forces, which greatly simplifies a discussion of Onsager symmetry.

The Chapman–Enskog algorithm<sup>(12,16,17)</sup> is a perturbation scheme that treats the streaming operator  $\mathcal{S}$  as a small perturbation of  $\mathcal{R}$  in (2.3). For clarity we introduce a formal expansion parameter  $\mu$  and write (2.3) in the form

$$\frac{\partial}{\partial t} P(\mathbf{v}, \mathbf{r}, t) = (\mu^{-1}\mathcal{R} + \mathcal{S})P(\mathbf{v}, \mathbf{r}, t) \quad (3.3)$$

(the parameter  $\mu$  should be put equal to unity in the final results). The normal solutions we are interested in have the form

$$P^{[\text{CE}]}(\mathbf{v}, \mathbf{r}, t) = P_{\text{eq}}(\mathbf{v}, \mathbf{r}) + \sum_{i=0}^4 c_i(\mathbf{r}, t)\phi_i(\mathbf{v}) + h(\mathbf{v}, \mathbf{r}, t) \quad (3.4)$$

where

$$h(\mathbf{v}, \mathbf{r}, t) = \sum_{k=1}^{\infty} \mu^k h^{(k)}(\mathbf{v}, \mathbf{r}, t) \quad (3.5)$$

is a linear combination of the  $\phi_i(\mathbf{v})$  with  $i > 4$  with coefficients that are linear functionals of the  $\mathbf{c}(\mathbf{r}, t)$  in (3.4). Substitution of (3.4) into (3.3) and scalar multiplication with the first five moments  $\phi_i(\mathbf{v})$  yields the moment equations

$$\begin{aligned} \frac{\partial}{\partial t} c_0(\mathbf{r}, t) &= -\partial \cdot \mathbf{c} \\ \frac{\partial}{\partial t} \mathbf{c}(\mathbf{r}, t) &= -\frac{1}{m\beta} \mathbf{D}c_0 - \frac{2}{3m} \partial c_4 - \frac{1}{m} \partial \cdot \mathbf{P} \\ \frac{\partial}{\partial t} c_4(\mathbf{r}, t) &= -\frac{1}{\beta} \mathbf{D} \cdot \mathbf{c} - \partial \cdot \mathbf{q} \end{aligned} \quad (3.6)$$



where we used the abbreviations

$$\partial = \partial/\partial\mathbf{r}; \quad \mathbf{D} = \partial + \beta \partial\Phi/\partial\mathbf{r} \quad (3.7)$$

The excess pressure tensor  $\mathbf{P}$  and the heat current  $\mathbf{q}$  are defined as

$$\mathbf{P}(\mathbf{r}, t) = \int d\mathbf{v} m\mathbf{v}\mathbf{v}h(\mathbf{v}, \mathbf{r}, t) \quad (3.8)$$

$$\mathbf{q}(\mathbf{r}, t) = \int d\mathbf{v} \frac{1}{2}mv^2\mathbf{v}h(\mathbf{v}, \mathbf{r}, t)$$

Substitution of successive terms from (3.5) into (3.8) and (3.6) yields successive approximations to the evolution operator matrix  $\mathbf{M}$  in (3.1). Inclusion of terms up to order zero, one, and two gives the linearized Euler, Navier–Stokes, and Burnett equations, respectively.<sup>3</sup> The explicit forms are given in the Appendix.

In order to inspect the Onsager symmetry of the equations so obtained, we recast (3.1) into the form

$$\frac{\partial}{\partial t} \mathbf{c}(\mathbf{r}, t) = \mathbf{L} \cdot n_{\text{eq}}(\mathbf{r}) \mathbf{f}(\mathbf{r}, t) \quad (3.9)$$

The thermodynamic forces  $\mathbf{f}(\mathbf{r}, t)$  are the functional derivatives with respect to the  $\mathbf{c}(\mathbf{r}, t)$  of the second-order entropy functional obtained by substituting (3.4) into  $S^{[2]}[P]$  defined by (2.10). Since the  $c_i(\mathbf{r}, t)$  with  $i > 4$  that result from expanding  $h(\mathbf{v}, \mathbf{r}, t)$  in (3.4) in terms of the  $\phi_k(\mathbf{v})$  are linear functionals of the  $\mathbf{c}(\mathbf{r}, t)$ , this results in a bilinear functional in the  $\mathbf{c}$ ; after some integrations by parts this functional can be written as

$$S^{[2]}[\mathbf{c}] = -\frac{1}{2}k \int d\mathbf{r} n_{\text{eq}}^{-1}(\mathbf{r}) \mathbf{c}(\mathbf{r}) \cdot \mathbf{G} \cdot \mathbf{c}(\mathbf{r}) \quad (3.10)$$

from which the set of thermodynamic forces follow as

$$\mathbf{f} = kn_{\text{eq}}^{-1} \mathbf{G} \cdot \mathbf{c} \quad (3.11)$$

Since the term  $h$  in (3.4) enters into the calculation of  $\mathbf{G}$  as a power series in  $\mu$ , one obtains a power series for  $\mathbf{G}$  as well. In zeroth order the results (2.11) for  $i \leq 4$  are recovered, but in order  $\mu^2$  there appears a correction term; its explicit form is given in the Appendix. (The resulting correction

<sup>3</sup> These designations differ somewhat from those found in the literature. The customary forms are obtained by substituting (3.2), performing an additional linearization in terms of the fields  $\delta n(\mathbf{r}, t)$ ,  $\mathbf{u}(\mathbf{r}, t)$ , and  $\delta T(\mathbf{r}, t)$ , and extracting evolution equations for these fields.

terms of  $f$  were overlooked in Ref. 5.) From the power series in  $\mu$  for  $\mathbf{M}$  and  $\mathbf{G}$  a series for the operator matrix  $\mathbf{L}$  defined in (3.9) can be obtained. The Onsager–Casimir symmetry requirements for this operator matrix are, in full analogy with (2.16),

$$\mathcal{L}_{\alpha\beta} = \eta_\alpha \eta_\beta \mathcal{L}_{\beta\alpha}^+, \quad \alpha, \beta = 0, \dots, 4 \tag{3.12}$$

with

$$\eta_0 = \eta_4 = 1; \quad \eta_{1,2,3} = -1 \tag{3.13}$$

Using the explicit expressions from the Appendix, one obtains for  $\mathbf{L}$  up to order  $\mu$

$$k\mathbf{L} = k\mathbf{L}^{(0)} + \mu k\mathbf{L}^{(1)} = \frac{1}{m\beta} \begin{pmatrix} 0 & -\partial & 0 \\ -\mathbf{D} & \mathbf{0} & -\beta^{-1}\partial \\ 0 & -\beta^{-1}\mathbf{D} & 0 \end{pmatrix} + \mu \frac{\eta}{m} \begin{pmatrix} 0 & \mathbf{0} & 0 \\ \mathbf{0} & (1/m\beta)(\frac{1}{3}\partial\partial + \partial \cdot \partial \mathbf{l}) n_{\text{eq}}^{-1} & \mathbf{0} \\ 0 & \mathbf{0} & (5/2\beta^2 \text{Pr}) \partial \cdot \partial n_{\text{eq}}^{-1} \end{pmatrix} \tag{3.14}$$

where  $\eta$  denotes the viscosity and  $\text{Pr}$  the Prandtl number (A.13). In view of the relations

$$\partial n_{\text{eq}}^{-1} = n_{\text{eq}}^{-1} \mathbf{D}; \quad \partial^+ = -\mathbf{D} \tag{3.15}$$

which follow directly from the definition (3.7) and (2.17), this operator clearly satisfies the symmetry requirement (3.12).

The second-order correction is given by

$$k\mathbf{L}^{(2)} = \left(\frac{\eta}{m}\right)^2 \begin{pmatrix} 0 & \mathbf{l}_a & 0 \\ \mathbf{l}_b & \mathbf{0} & \mathbf{l}_c \\ 0 & \mathbf{l}_d & 0 \end{pmatrix} \tag{3.16}$$

with

$$\begin{aligned} \mathbf{l}_a &= -2(1 + z_1) n_{\text{eq}}^{-1} \mathbf{D} \mathbf{D} \cdot \partial n_{\text{eq}}^{-1}; & \mathbf{l}_b &= \mathbf{l}_a^+ \\ \mathbf{l}_c &= \mathbf{l}_1 - \mathbf{l}_2 - \mathbf{l}_3 - \mathbf{l}_4; & \mathbf{l}_d &= \mathbf{l}_1^+ + \mathbf{l}_2^+ + \mathbf{l}_3^+ - \mathbf{l}_4^+ \end{aligned} \tag{3.17a}$$

where

$$\begin{aligned} \beta \mathbf{l}_1 &= 2(1 + z_1) n_{\text{eq}}^{-1} \mathbf{D} n_{\text{eq}}^{-1} \cdot \overset{\circ}{\mathbf{D}} \overset{\circ}{\partial} \\ \beta \mathbf{l}_2 &= 2(\text{Pr})^{-1} (1 + z_2) n_{\text{eq}}^{-1} \mathbf{D} \cdot \overset{\circ}{\partial} \partial n_{\text{eq}}^{-1} \\ \beta \mathbf{l}_3 &= z_3 n_{\text{eq}}^{-1} \mathbf{D} \cdot \overset{\circ}{\mathbf{D}} \partial n_{\text{eq}}^{-1} \\ \beta \mathbf{l}_4 &= \frac{5}{3} (\text{Pr})^{-2} (1 + z_4) n_{\text{eq}}^{-1} \mathbf{D} \mathbf{D} \cdot \partial n_{\text{eq}}^{-1} \end{aligned} \tag{3.17b}$$

Here we used the notation  $\hat{\mathbf{A}}$  for the traceless part of the tensor  $\mathbf{A}$  and an overbar to denote the symmetric part of a tensor; the numbers  $z_1, \dots, z_4$  are related in the Appendix to certain matrix elements of the collision operator  $\mathcal{R}$ . From the definitions given there it follows that they vanish for Maxwell molecules and for the BGK model.

The Onsager–Casimir symmetry requirements (3.12) would imply for the vector operators defined in (3.16)

$$\mathbf{I}_b = -\mathbf{I}_a^+; \quad \mathbf{I}_d = -\mathbf{I}_c^+ \tag{3.18}$$

which is clearly not the case. Closer inspection shows that contributions involving  $z_2$  and  $z_3$  behave correctly, whereas those with  $z_1$  and  $z_4$  exhibit maximal violation. From the definitions (A.18) of the  $z_k$  one sees that  $z_1$  and  $z_4$  depend only on the even and the odd components of  $h(\mathbf{v}, \mathbf{r}, t)$ , respectively; hence, they also occur in the second-order contributions to  $G$ . In contrast,  $z_2$  and  $z_3$  depend on both even and odd components of  $h$  and do not occur in the second-order part of  $G$ . The salvaging procedure for the Onsager relations described in Refs. 7 and 8 involves a redefinition of the thermodynamic forces, and hence of  $G$ , in which components of  $P(\mathbf{v}, \mathbf{r}, t)$  with different parity are treated differently. Hence, we may expect the procedure to work in our case as well. As we show in the next section, this is indeed the case.

Our calculations reported in this section have basically confirmed the observation by McLennan.<sup>(5)</sup> We have shown in addition that the inclusion of an external potential and the retention of terms omitted after a linearization following the substitution (3.2) does not alter the order in  $\mu$  in which the violations of Onsager symmetry first occur. Finally, we have shown that the symmetry is not restored when one takes into account the correction terms to the thermodynamic forces neglected in Ref. 5, which are of the same order as the violations themselves.

#### 4. THE RESTORATION OF ONSAGER–CASIMIR SYMMETRY

As in Refs. 7 and 8, we now show that the Onsager–Casimir symmetry can be restored by a modification of the definition of the thermodynamic forces. For the modified treatment the fundamental thermodynamic quantity is not  $S[P]$ , but rather the associated Lagrangian-type quantity

$$\begin{aligned} \hat{S}[P] = & \frac{1}{2} k \int d\mathbf{r} \int d\mathbf{v} [P(\mathbf{v}, \mathbf{r}, t) + P(-\mathbf{v}, \mathbf{r}, t)] \\ & \times \ln[P(\mathbf{v}, \mathbf{r}, t)/P_{\text{eq}}(\mathbf{v}, \mathbf{r})] \end{aligned} \tag{4.1}$$

which, up to second order in the expansion coefficients  $c_i(\mathbf{r}, t)$ , equals

$$\hat{S}^{[2]}[P] = \frac{1}{2} k \sum_i \eta_i \alpha_i \int d\mathbf{r} [c_i(\mathbf{r}, t)]^2 n_{\text{eq}}^{-1}(\mathbf{r}) \tag{4.2}$$

The reformulation of the mesoscopic Onsager relations can now be carried through in complete analogy with Section 4 of I. In the hydrodynamic stage the  $c_i$  with  $i > 4$  cease to be independent variables;  $\hat{S}^{[2]}$  becomes a functional of the set of hydrodynamic fields  $\mathbf{c}(\mathbf{r}, t)$  and assumes the form

$$\hat{S}^{[2]}[\mathbf{c}] = -\frac{1}{2} k \int d\mathbf{r} n_{\text{eq}}^{-1}(\mathbf{r}) \mathbf{c}(\mathbf{r}) \cdot \hat{\mathbf{G}} \cdot \mathbf{c}(\mathbf{r}) \tag{4.3}$$

The explicit form of  $\hat{\mathbf{G}}$  is given in the Appendix. The modified thermodynamic forces  $\hat{\mathbf{f}}(\mathbf{r}, t)$  derived from  $\hat{S}^{[2]}[\mathbf{c}]$  are

$$\hat{\mathbf{f}} = -\delta S[\mathbf{c}]/\delta \mathbf{c} = k n_{\text{eq}}^{-1} \hat{\mathbf{G}} \cdot \mathbf{c} \tag{4.4}$$

The operator matrix  $\hat{\mathbf{L}}$  defined by the relation

$$\frac{\partial}{\partial t} \mathbf{c} = \mathbf{M} \cdot \mathbf{c} = k \hat{\mathbf{L}} \cdot \hat{\mathbf{G}} \cdot \mathbf{c} = \hat{\mathbf{L}} \cdot n_{\text{eq}} \hat{\mathbf{f}} \tag{4.5}$$

should then obey the Onsager–Casimir symmetry relations

$$\mathcal{L}_{\mu\nu} = \mathcal{L}_{\nu\mu}^+ \tag{4.6}$$

These relations are indeed satisfied by the explicit expressions obtained in our calculations: from the results for  $\mathbf{M}$  and  $\mathbf{G}$  in the Appendix one obtains up to order  $\mu^2$

$$\begin{aligned} k\hat{\mathbf{L}} = & \frac{1}{m\beta} \begin{pmatrix} 0 & -\partial & 0 \\ \mathbf{D} & \mathbf{0} & \beta^{-1}\partial \\ 0 & -\beta^{-1}\mathbf{D} & 0 \end{pmatrix} + \mu \begin{pmatrix} 0 & \mathbf{0} & 0 \\ \mathbf{0} & \mathbf{L} & \mathbf{0} \\ 0 & \mathbf{0} & -\mathcal{L}_{44} \end{pmatrix} \\ & + \mu^2 \left(\frac{\eta}{m}\right)^2 \begin{pmatrix} 0 & -\mathbf{l}_a & 0 \\ -\mathbf{l}_b & \mathbf{0} & \hat{\mathbf{l}}_c \\ 0 & \hat{\mathbf{l}}_d & 0 \end{pmatrix} \end{aligned} \tag{4.7}$$

where  $\mathbf{L}$  and  $\mathcal{L}_{44}$  denote the corresponding parts of  $\mathbf{L}^{(1)}$  in (3.14),  $\mathbf{l}_a$  and  $\mathbf{l}_b$  are defined in (3.17a), while  $\hat{\mathbf{l}}_c$  and  $\hat{\mathbf{l}}_d$  are given by

$$\hat{\mathbf{l}}_c = -\mathbf{l}_1 + \mathbf{l}_2 + \mathbf{l}_3 - \mathbf{l}_4; \quad \hat{\mathbf{l}}_d = -\mathbf{l}_1^+ + \mathbf{l}_2^+ + \mathbf{l}_3^+ - \mathbf{l}_4^+ \tag{4.8}$$

with  $\mathbf{l}_{1,\dots,4}$  defined in (3.17b). The requirements

$$-\mathbf{l}_a = -\mathbf{l}_b^+; \quad \hat{\mathbf{l}}_c = \hat{\mathbf{l}}_d^+ \tag{4.9}$$

which follow from (4.6), are clearly fulfilled, as are the corresponding requirements for the first two terms in (4.7). Thus, at least up to order  $\mu^2$ , the redefinition of the thermodynamic forces does indeed enable the Onsager–Casimir symmetry to survive the elimination of fast variables via the Chapman–Enskog algorithm.

The classical Onsager relations imply<sup>(15)</sup> that eigenfunctions of the evolution operator  $M$  with different eigenvalues are orthogonal with respect to the weight  $n_{\text{eq}}^{-1} \mathbf{G} \cdot \mathbf{U}$ , where  $\mathbf{U}$  is defined by

$$U_{\mu\nu} = \delta_{\mu\nu} \eta_\nu \tag{4.10}$$

The modified Onsager relations imply orthogonality with respect to  $-n_{\text{eq}}^{-1} \hat{\mathbf{G}}$ , which differs from  $n_{\text{eq}}^{-1} \mathbf{G} \cdot \mathbf{U}$  in order  $\mu^2$ . The former orthogonality property was used by Titulaer and Felderhof<sup>(14)</sup> to prove the Lekkerkerker–Laidlaw relation.<sup>(5,13)</sup> This relation states that the number  $n_*$  of complex eigenvalues of the linear evolution operator of a system with  $n_+$  even and  $n_-$  odd variables obeys the inequality

$$n_* \leq 2 \min(n_+, n_-) \tag{4.11}$$

Of course, this relation is not directly relevant to our system, which has an infinite number of variables. However, in a homogeneous system  $M$  can be reduced to a direct product of finite-dimensional matrices by a spatial Fourier transformation, and (4.11) becomes relevant. Inspection of the proof in Ref. 14 shows that it remains valid for the modified Onsager relations as long as the restrictions of  $\hat{\mathbf{G}}$  to the subspaces of odd and even variables remain positive- and negative-definite, respectively. The same conclusion emerges when one tries to adapt the original proof.<sup>(13)</sup> This can be done by introducing the operator matrix

$$\mathbf{Q} = -k^{-1} n_{\text{eq}}^{-1/2} (-\mathbf{U} \cdot \hat{\mathbf{G}})^{1/2} \cdot \mathbf{M} \cdot (-\mathbf{U} \cdot \hat{\mathbf{G}})^{-1/2} n_{\text{eq}}^{1/2} \tag{4.12}$$

that is the analog of the operator  $\mathcal{Q}$  introduced in Section 4 of I. By construction,  $\mathbf{Q}$  is similar to  $\mathbf{M}$ . Substitution of  $\mathbf{M} = k \hat{\mathbf{L}} \cdot \hat{\mathbf{G}} = k \hat{\mathbf{L}} \cdot \mathbf{U} \cdot \mathbf{U} \cdot \hat{\mathbf{G}}$  [cf. (4.5)] leads to

$$\mathbf{Q} = n_{\text{eq}}^{-1/2} (-\mathbf{U} \cdot \hat{\mathbf{G}})^{1/2} \cdot \hat{\mathbf{L}} \cdot \mathbf{U} \cdot (-\mathbf{U} \cdot \hat{\mathbf{G}})^{1/2} n_{\text{eq}}^{1/2} \tag{4.13}$$

Using the relations  $\hat{\mathbf{L}} = \hat{\mathbf{L}}^+$  and  $\hat{\mathbf{G}} = \hat{\mathbf{G}}^+$ , the lemma (I.4.19), and the fact that  $\hat{\mathbf{G}}$  and  $\mathbf{U}$  commute [the latter is obvious in (4.2); the relation must

remain valid when the expressions for the  $c_i(\mathbf{r}, t)$  with  $i > 4$  from the Chapman–Enskog algorithm are inserted], one arrives at the relation

$$\mathbf{Q}^{\dagger} = \mathbf{U} \cdot \mathbf{Q} \cdot \mathbf{U} \quad (4.14)$$

The existence of such a relation for a  $\mathbf{Q}$  similar to  $\mathbf{M}$  was the starting point for the proof in Ref. 13. The proof again obviously breaks down when  $-\mathbf{U} \cdot \hat{\mathbf{G}}$  ceases to be positive-definite.

## 5. CONCLUDING REMARKS

In any discussion of Onsager–Casimir symmetry relations it is crucial to use a correct, consistent set of thermodynamic forces and fluxes. Consistency is guaranteed when the forces and fluxes are derived from a set of thermodynamic variables. (For open systems, an appropriate thermodynamic function, such as the Helmholtz or Gibbs free energy, should of course be used instead of the entropy.) One has considerable freedom in choosing the set of thermodynamic variables, but they should provide a complete and nonredundant specification of the state of the system at the chosen level of description. Thus, in particular, the number of forces or fluxes should always be equal to the number of independent variables in the system at that chosen level.

Of course, any relation that is true because of Onsager symmetry at the mesoscopic level remains a valid relation at the hydrodynamic level. Thus, one may substitute the Chapman–Enskog results for the  $c_i(\mathbf{r}, t)$  with  $i > 4$  into the expression (2.18) for the mesoscopic fluxes, and decompose the results with respect to the similarly obtained Chapman–Enskog values of the mesoscopic forces. The expansion coefficients so obtained should then obey Onsager symmetry. However, the decomposition discussed will not be unique, since all  $f_i(\mathbf{r}, t)$  can ultimately be derived from the hydrodynamic fields  $c(\mathbf{r}, t)$  by differentiations and multiplications with derivatives of  $\Phi(\mathbf{r})$ , and the operator  $\mathcal{S}$  in (2.18) contains just these operations. A decomposition in terms of the mesoscopic forces does become unique, however, even in the hydrodynamic stage, if one requires the coefficients to be functions (not operators) that depend on  $\Phi(\mathbf{r})$  via the equilibrium density, but do not contain derivatives of  $\Phi(\mathbf{r})$  as explicit factors. This procedure would not recover the mesoscopic Onsager matrix for the full fluxes, but it is correct for the dissipative parts of the fluxes, as is clear from the expression (2.21). A formalism of this type is presented by Kuščer<sup>(11)</sup> in the course of a more general discussion of the incorporation of Burnett effects into irreversible thermodynamics. The fluxes defined in (K.19–22)<sup>4</sup> are, up to numerical factors and linear combinations of

<sup>4</sup> The notation (K.x) refers to Eq. (x) in Ref. 11.

quantities with the same tensorial character, precisely the *dissipative* fluxes associated with the mesoscopic variables

$$\tilde{c}_i(\mathbf{r}, t) = \int d\mathbf{v} P(\mathbf{v}, \mathbf{r}, t) \mathcal{R}^{-1} \Psi^i(\mathbf{v}) \quad (5.1)$$

with the  $\Psi^i$  defined in (K.12–15), as is readily seen using (2.21) and (K.11). The dissipative nature of the fluxes is also apparent from the fact that the Onsager matrix (K.23–27), unlike, e.g., our (3.14) and (3.16), couples only quantities with the same parity.

Of course, for the analysis given in Ref. 11, which is restricted to stationary systems, it is essential to consider the dissipative fluxes, rather than the full fluxes, which vanish identically. The symmetry properties of the matrix in (K.23–27) indeed originate in Onsager relations, albeit mesoscopic ones, but they involve only a subset of all mesoscopic Onsager–Casimir relations; their validity requires microscopic reversibility for the scattering process only, rather than of the full Boltzmann dynamics.

In our discussion of Onsager symmetry we have constructed the hydrodynamic evolution equations, as well as the entropy and its Lagrangian, from the mesoscopic description of the system. In practice, however, Onsager symmetry is often invoked to constrain one’s freedom in choosing the coefficients in a *phenomenological* ansatz for the equations of motion. As is clear from our discussion in Section 3, such a procedure requires, in addition to the ansatz for the equations of motion, a phenomenological ansatz for the second-order entropy  $S^{[2]}[c]$  that includes contributions from higher gradients of the hydrodynamic fields (up to the order considered in the equations of motion). Similarly, the use of the modified Onsager–Casimir relations discussed in Section 4 requires an ansatz for the second-order entropy Lagrangian  $\hat{S}^{[2]}[c]$ . A comparison of the kinetically derived expressions in the Appendix shows that  $\hat{S}^{[2]}$  contains the same terms as  $S^{[2]}$ , but often with different signs. Such a relation should also hold for the analogous phenomenological expressions. The correct signs to use in  $\hat{S}^{[2]}$  are probably best determined by comparison with a kinetically derived expression; for some cases, such as bulk viscosity terms and their Burnett analogs, the kinetic equation to use will be the Enskog equation rather than the Boltzmann equation.<sup>5</sup>

Though the entropy Lagrangian has a less immediate physical interpretation than the entropy itself, it is, at least in principle, a measurable quantity: it determines the “slipped” initial conditions for the correlation

<sup>5</sup> A recent discussion of entropy functionals for the Enskog equation can be found in Ref. 18.

functions of the hydrodynamic fields. By applying the theory of Sections 5 and 6 of Ref. 7, or by a comparison with Ref. 5, one can prove the relation

$$\langle \mathbf{c}(\mathbf{r}, 0 + \varepsilon), \mathbf{c}(\mathbf{r}', 0) \rangle_r = (-\mathbf{U} \cdot \hat{\mathbf{G}})^{-1} \delta(\mathbf{r} - \mathbf{r}') \quad (5.2)$$

where  $\varepsilon$  denotes a time large on the mesoscopic scale, but small on the hydrodynamic scale; the average  $\langle \dots, \dots \rangle_r$ , defined in (2.17), coincides with the thermal equilibrium average. More formally, one can write, following McLennan,<sup>(5)</sup>

$$\langle \mathbf{c}(\mathbf{r}, 0 + \varepsilon), \mathbf{c}(\mathbf{r}', 0) \rangle_r = \lim_{t \downarrow 0} \exp[-Mt] \cdot \langle \mathbf{c}(\mathbf{r}, t), \mathbf{c}(\mathbf{r}', 0) \rangle_r \quad (5.3)$$

McLennan<sup>(5)</sup> also shows how the correlation function in (5.2) can be extracted, at least for homogeneous systems, from the high-frequency behavior of dynamic scattering functions. It is also clear from (5.2) that the appearance of a zero eigenvalue of  $-\mathbf{U} \cdot \hat{\mathbf{G}}$ , which signals the breakdown of some of the procedures described in Section 4, also signifies a breakdown of the separation between mesoscopic and hydrodynamic time scales.

Throughout this paper we have assumed the validity of the hydrodynamic description everywhere in the system. This may be correct when the spatial confinement is effected by a potential  $\Phi(\mathbf{r})$  that is smooth on the scale of a mean free path. In view of the density dependence of the mean free path, this is a rather severe restriction for the regions where  $\beta\Phi(\mathbf{r})$  is large. Nevertheless, this possibility was one of our reasons to include the potential terms in our treatment, in spite of the additional complications in the formulas.

A more complicated situation arises when the system is confined by walls. Then, for many mesoscopic boundary conditions, kinetic boundary layers of a thickness of a few mean free paths occur. The structure of these boundary layers determines the boundary conditions that should be imposed on the solutions of the hydrodynamic equations.<sup>(6,19)</sup> Since  $P(\mathbf{v}, \mathbf{r}, t)$  no longer has the Chapman-Enskog form inside the boundary layer, such layers also cause additional contributions to the mesoscopic entropy (and entropy Lagrangian) density, and singular boundary terms in their macroscopic analogues. One may expect that a study of the Onsager symmetry properties of these singular terms will lead to relations between the accommodation coefficients appearing in the boundary conditions for the hydrodynamic fields. A few further remarks on this topic, and more generally on the relevance of the Burnett equations for systems with kinetic boundary layers, can be found in the paper by Kuščer.<sup>(11)</sup> A more complete and specific discussion would clearly exceed the scope of the present paper.



APPENDIX

In this Appendix we sketch the calculations leading to the expressions for the matrix operators  $L$  and  $\hat{L}$  in Sections 3 and 4. The calculations follow the familiar Chapman–Enskog procedure, but because of our choice of variables and our inclusion of contributions from an external potential, they cannot be found as such in the literature. Our starting point is the Boltzmann equation, written in the form

$$\frac{\partial}{\partial t} P^{[CE]}(\mathbf{v}, \mathbf{r}, t) = (\mathcal{S} + \mu^{-1}\mathcal{R}) P^{[CE]}(\mathbf{v}, \mathbf{r}, t) \tag{A.1}$$

where  $P^{[CE]}$  is specified in (3.4) and (3.5) and the operators  $\mathcal{S}$  and  $\mathcal{R}$  in (2.3). The  $P^{[CE]}$  depends on  $t$  via the hydrodynamic fields  $\mathbf{c}(\mathbf{r}, t)$ , which obey a set of coupled equations of the form

$$\frac{\partial}{\partial t} \mathbf{c}(\mathbf{r}, t) = \mathbf{M} \cdot \mathbf{c} = \left[ \sum_{k=0}^{\infty} \mu^k \mathbf{M}^{(k)} \right] \cdot \mathbf{c} \tag{A.2}$$

One need not include a term of order  $\mu^{-1}$  in  $\mathbf{M}$ , since the parts of  $P^{[CE]}$  other than  $h(\mathbf{v}, \mathbf{r}, t)$  in (3.4) are annihilated by  $\mathcal{R}$ . The structure of  $\mathbf{M}$  is given in (3.6); the quantities  $\mathbf{P}$  and  $\mathbf{q}$  can be written as

$$\mathbf{P}(\mathbf{r}, t) = \sum_{k=1}^{\infty} \mu^k \mathbf{P}^{(k)}(\mathbf{r}, t); \quad \mathbf{q}(\mathbf{r}, t) = \sum_{k=1}^{\infty} \mu^k \mathbf{q}^{(k)}(\mathbf{r}, t) \tag{A.3}$$

with

$$\mathbf{P}^{(k)} = \langle \mathbf{F}_p, h^{(k)} \rangle_{\mathbf{v}}; \quad \mathbf{q}^{(k)} = \langle \mathbf{f}_q, h^{(k)} \rangle_{\mathbf{v}} \tag{A.4}$$

$$\mathbf{F}_p(\mathbf{v}) = m\mathbf{v}\mathbf{v}\phi_0(\mathbf{v}); \quad \mathbf{f}_q(\mathbf{v}) = \left( \frac{m}{2} v^2 - \frac{5}{2\beta} \right) \mathbf{v}\phi_0(\mathbf{v}) \tag{A.5}$$

The scalar product in (A.4) is defined in (2.4). These expressions are equivalent to (3.8); the addition of the superscript  $\circ$  in  $\mathbf{F}_p$  is immaterial, since  $h$  is orthogonal to  $\frac{1}{2}mv^2\phi_0$ . Similarly, the additional term in  $\mathbf{f}_q$  is immaterial because of the required orthogonality to  $\mathbf{v}\phi_0$ .

The lowest order contribution to  $\mathbf{M}$  can be read off directly from (3.6):

$$\mathbf{M}^{(0)} = \begin{pmatrix} 0 & -\partial & 0 \\ -(1/m\beta) \mathbf{D} & \mathbf{0} & -(2/3m) \partial \\ 0 & -(1/\beta) \mathbf{D} & 0 \end{pmatrix} \tag{A.6}$$

The determining equation for  $h^{(1)}$  obtained via the customary Chapman–Enskog procedure<sup>(12,16,17)</sup> reads

$$\mathcal{R}h^{(1)} = \frac{2}{3} \beta^2 \mathbf{f}_q \cdot \mathbf{D}c_4 + \beta \mathbf{F}_P : \mathbf{D}c \tag{A.7}$$

Since the rhs of (A.7) is orthogonal to the null space of  $\mathcal{R}$ , this equation can be solved. Since, moreover,  $\mathcal{R}$  and hence  $\mathcal{R}^{-1}$  preserve the tensorial character of any function of  $\mathbf{v}$ , the solution can be written as

$$h^{(1)} = n_{\text{eq}}^{-1} \left[ \frac{2}{3} \beta A(v^2) \mathbf{v} \cdot \mathbf{D}c_4 + m \beta B(v^2) \mathbf{v}\mathbf{v} : \mathbf{D}c \right] \phi_0(\mathbf{v}) \tag{A.8}$$

where  $A(v^2)$  and  $B(v^2)$  are defined via the relations

$$A(v^2) \mathbf{v}\phi_0 = \beta n_{\text{eq}} \mathcal{R}^{-1} \mathbf{f}_q, \quad B(v^2) \mathbf{v}\mathbf{v}\phi_0 = m^{-1} n_{\text{eq}} \mathcal{R}^{-1} \mathbf{F}_P \tag{A.9}$$

As is customary, we expand  $A$  and  $B$  in terms of the Sonine polynomials, defined in Ref. 16<sup>6</sup>:

$$A(v^2) = \sum_{r=1}^{\infty} a_r S_{3/2}^{(r)} \left( \frac{1}{2} m \beta v^2 \right); \quad B(v^2) = \sum_{r=0}^{\infty} b_r S_{5/2}^{(r)} \left( \frac{1}{2} m \beta v^2 \right) \tag{A.10}$$

(there is no term with  $a_0$ , since  $h$  should be orthogonal to  $\mathbf{v}\phi_0$ ). For Maxwell molecules and for the BGK model the series in (A.10) consist of their lowest term only.<sup>(17)</sup> By substituting (A.8) and (A.10) into (A.4) and using the properties of the Sonine polynomials, one obtains

$$\mathbf{q}^{(1)} = -\frac{5}{3} \frac{a_1}{m\beta} n_{\text{eq}}^{-1} \mathbf{D}c_4 \equiv -\frac{2}{3k} \lambda n_{\text{eq}}^{-1} \mathbf{D}c_4 \tag{A.11}$$

$$\mathbf{P}^{(1)} = 2b_0 \beta^{-1} n_{\text{eq}}^{-1} \overline{\mathbf{D}c} \equiv -2\eta n_{\text{eq}}^{-1} \overline{\mathbf{D}c} \tag{A.12}$$

where we introduced the heat conductivity  $\lambda$  and viscosity  $\eta$ . With these one can form the dimensionless Prandtl number

$$\text{Pr} = \eta c_p / \lambda = \frac{5}{2} k \eta / m \lambda \tag{A.13}$$

Insertion of (A.11)–(A.13) into (3.6) gives the first-order contribution to  $\mathbf{M}$ :

$$\mathbf{M}^{(1)} = \frac{\eta}{m} n_{\text{eq}}^{-1} \begin{pmatrix} 0 & \mathbf{0} & 0 \\ \mathbf{0} & \frac{1}{3} \mathbf{D}\mathbf{D} + \mathbf{D} \cdot \mathbf{D}\mathbf{l} & \mathbf{0} \\ 0 & \mathbf{0} & (5/3 \text{ Pr}) \mathbf{D} \cdot \mathbf{D} \end{pmatrix} \tag{A.14}$$

<sup>6</sup> Due to the factor  $n_{\text{eq}}$  introduced in (A.9), the  $a_r$  and  $b_r$  are independent of the equilibrium density (which in our case depends on position). In this respect our definition differs from the one used, e.g., in Ref. 16.

For the second-order contribution to  $h$  we obtain the equation

$$\begin{aligned} \mathcal{R}h^{(2)} = & \left\{ n_{\text{eq}}^{-1} \left[ -2b_0 \mathbf{D} \cdot \overset{\circ}{\mathbf{D}}\mathbf{c} \cdot \mathbf{v} + \frac{10}{9} \frac{a_1}{m} \left( \frac{1}{2} m\beta v^2 - \frac{3}{2} \right) \mathbf{D} \cdot \mathbf{D}c_4 \right. \right. \\ & - \frac{2\beta}{3m} A\Phi' \cdot \mathbf{D}c_4 \left. \right] + \frac{2}{3} \beta \mathbf{v}\mathbf{v}: (\mathbf{A}\mathbf{D} - \beta A'\Phi') n_{\text{eq}}^{-1} \mathbf{D}c_4 \\ & - n_{\text{eq}}^{-1} B\overset{\circ}{\mathbf{v}}\mathbf{v}: \left( \mathbf{D}\overset{\circ}{\mathbf{D}}c_0 + \frac{2}{3} \beta \mathbf{D}\overset{\circ}{\partial}c_4 \right) + \left[ -2\beta B\Phi' \cdot \overset{\circ}{\partial}\mathbf{c} \cdot \mathbf{v} \right. \\ & \left. \left. + m\beta (\mathbf{B}\mathbf{D} - \beta B'\Phi') \cdot \mathbf{v} (\overset{\circ}{\mathbf{v}}\mathbf{v}: \overset{\circ}{\partial}\mathbf{c}) - \frac{2}{3} A\mathbf{v} \cdot \overset{\circ}{\partial}\mathbf{c} \cdot \mathbf{c} \right] n_{\text{eq}}^{-1} \right\} \phi_0 \quad (\text{A.15}) \end{aligned}$$

where  $\Phi'$  denotes  $\partial\Phi$ , while  $A'$  and  $B'$  denote derivatives with respect to the argument of the Sonine polynomials of  $A$  and  $B$ . By construction, the rhs of (A.15) is orthogonal to the null space of  $\mathcal{R}$ , hence  $h^{(2)}$  can be obtained by applying  $\mathcal{R}^{-1}$  to it. Fortunately, for the calculation of  $\mathbf{P}^{(2)}$  and  $\mathbf{q}^{(2)}$  one need not evaluate the resulting expression; instead, one exploits the Hermiticity of  $\mathcal{R}^{-1}$  and uses the definitions (A.9) and (A.4). Inserting the expansions (A.10) and exploiting the recursion and orthogonality properties of the Sonine polynomials,<sup>(20)</sup> one obtains results that can be written in the form

$$\begin{aligned} \mathbf{q}^{(2)} = & \frac{\eta^2}{m} n_{\text{eq}}^{-1} \left[ \frac{2}{\text{Pr}} (1+z_2) \mathbf{D} \cdot \overset{\circ}{\partial}\mathbf{c} + z_3 \overset{\circ}{\partial} \cdot \overset{\circ}{\partial}\mathbf{c} \right. \\ & \left. - \frac{5}{3} (\text{Pr})^{-2} (1+z_4) \overset{\circ}{\partial}\mathbf{c} \cdot \mathbf{c} \right] n_{\text{eq}}^{-1} \quad (\text{A.16}) \end{aligned}$$

$$\begin{aligned} \mathbf{P}^{(2)} = & \frac{\eta^2}{m} n_{\text{eq}}^{-1} \left\{ -n_{\text{eq}}^{-1} (1+z_1) \left( 2\mathbf{D}\overset{\circ}{\mathbf{D}}c_0 + \frac{4}{3} \beta \overset{\circ}{\mathbf{D}}\overset{\circ}{\partial}c_4 \right) \right. \\ & \left. + \left[ \frac{4\beta}{3\text{Pr}} (1+z_2) \overset{\circ}{\partial}\overset{\circ}{\partial}c_4 + \frac{2}{3} \beta z_3 \overset{\circ}{\mathbf{D}}\overset{\circ}{\partial}c_4 \right] n_{\text{eq}}^{-1} \right\} \quad (\text{A.17}) \end{aligned}$$

where we introduced the abbreviations

$$\begin{aligned} z_1 &= \frac{1}{15} \sum_{r=1}^{\infty} \left( \frac{b_r}{b_0} \right)^2 \frac{(2r+5)!!}{2^r r!} \\ z_2 &= \frac{1}{15} \sum_{r=1}^{\infty} \frac{a_{r+1} b_r}{a_1 b_0} \frac{(2r+5)!!}{2^r r!} \\ z_3 &= \frac{2}{15} \sum_{r=1}^{\infty} \frac{a_r b_r}{(b_0)^2} \frac{(2r+5)!!}{2^r r!} \\ z_4 &= \frac{2}{15} \sum_{r=2}^{\infty} \left( \frac{a_r}{a_1} \right)^2 \frac{(2r+3)!!}{2^r r!} \end{aligned} \quad (\text{A.18})$$

For Maxwell molecules and for the BGK model all  $a_r$  with  $r > 1$  and all  $b_r$  with  $r > 0$  vanish; hence, all  $z_k$  in (A.18) vanish as well. Thus, the results for these special cases can be obtained from our general expressions by substitutions

$$z_k = 0, \quad \text{Pr} = 2/3 \quad (\text{Maxwell}) \quad (\text{A.19})$$

$$z_k = 0, \quad \text{Pr} = 1 \quad (\text{BGK}) \quad (\text{A.20})$$

Substitution of the results (A.16), (A.17) into (3.6) now yields an expression for  $M^{(2)}$  that can be written as

$$M^{(2)} = \left( \frac{\eta}{m} \right)^2 \begin{pmatrix} 0 & \mathbf{0} & 0 \\ \mathbf{l}_b & \mathbf{0} & \mathbf{m}_c \\ 0 & \mathbf{m}_d & 0 \end{pmatrix} \quad (\text{A.21})$$

where  $\mathbf{l}_b$  is given in (3.17a) and

$$\mathbf{m}_c = \frac{2}{3}\beta^2(\mathbf{l}_1 - \mathbf{l}_2 - \mathbf{l}_3); \quad \mathbf{m}_d = m\beta(\mathbf{l}_2^+ + \mathbf{l}_3^+ - \mathbf{l}_4^+) \quad (\text{A.22})$$

with  $\mathbf{l}_1, \dots, \mathbf{l}_4$  given by (3.17b).

In order to construct from  $M$  the associated Onsager operator matrix  $L$ , we need the entropy functional  $S^{[2]}[c]$ , which is constructed from  $S^{[2]}[P]$  in (2.10) by substituting the Chapman-Enskog solution (3.4). To zeroth order the part  $h(\mathbf{v}, \mathbf{r}, t)$  does not contribute and the result is readily cast into the form (3.10), with

$$G^{(0)} = \begin{pmatrix} 1 & \mathbf{0} & 0 \\ \mathbf{0} & m\beta\mathbf{1} & \mathbf{0} \\ 0 & \mathbf{0} & \frac{2}{3}\beta^2 \end{pmatrix} \quad (\text{A.23})$$

Since  $h$  is a linear combination of  $\phi_i$  with  $i > 4$ , there are no cross terms between  $h$  and the other parts of  $P^{[CE]}$ . The contributions from  $h$  can be written in the alternative form

$$\Delta S^{[2]}[h] = \frac{1}{2}k \langle h(\mathbf{v}, \mathbf{r}, t), h(\mathbf{v}, \mathbf{r}, t) \rangle_{r,v} \quad (\text{A.24})$$

where the scalar product is defined in (2.5). The form (A.24) can be derived by expansion from (2.9) using (2.5) and (2.1). The lowest order contribution is of order  $\mu^2$  and can be derived by substituting (A.8) for both functions  $h$  in (A.24). The angular part of the  $\mathbf{v}$  integrations in the scalar product can be carried out immediately; the remaining integral over  $|\mathbf{v}|$  requires insertion of (A.10) and use of recursion relations and orthogonality properties of the Sonine polynomials.<sup>(20)</sup> The resulting

expression is then brought into the form (3.10) via an integration by parts. For the second-order contribution to  $\mathbf{G}$  we thus obtain

$$\mathbf{G}^{(2)} = \left(\frac{\eta}{m}\right)^2 \begin{pmatrix} 0 & \mathbf{0} & 0 \\ \mathbf{0} & \mathbf{G} & \mathbf{0} \\ 0 & \mathbf{0} & \mathcal{G}_{44} \end{pmatrix} \tag{A.25}$$

with

$$\begin{aligned} \mathbf{G} &= -(m\beta)^2(1+z_1) n_{\text{eq}}^{-1} (2\overline{\mathbf{D}}\overline{\partial} - \frac{2}{3}\mathbf{D}\partial + \mathbf{D} \cdot \partial \mathbf{I}) n_{\text{eq}}^{-1} \\ \mathcal{G}_{44} &= -\frac{10}{9}m\beta^3(\text{Pr})^{-2}(1+z_4) n_{\text{eq}}^{-1} \mathbf{D} \cdot \partial n_{\text{eq}}^{-1} \end{aligned} \tag{A.26}$$

and  $z_1$  and  $z_4$  defined in (A.18).

To construct the matrix  $\hat{\mathbf{G}}$  occurring in the entropy Lagrangian (4.3), we must change the signs of all contributions to  $\mathbf{G}$  that originate in even parts of  $P^{[\text{CE}]}$ . From (A.8) one sees that the  $A$  part of  $h^{(1)}$  is odd, while the  $B$  part is even. From (A.26) and (A.18) one sees that  $\mathcal{G}_{44}$  originates from the  $A$  part, while  $\mathbf{G}$  originates from the  $B$  part. The expression for  $\hat{\mathbf{G}}$  is therefore

$$\hat{\mathbf{G}} = \begin{pmatrix} -1 & \mathbf{0} & 0 \\ \mathbf{0} & m\beta \mathbf{I} & \mathbf{0} \\ 0 & \mathbf{0} & -\frac{2}{3}\beta^2 \end{pmatrix} + \mu^2 \left(\frac{\eta}{m}\right)^2 \begin{pmatrix} 0 & \mathbf{0} & 0 \\ \mathbf{0} & -\mathbf{G} & \mathbf{0} \\ 0 & \mathbf{0} & \mathcal{G}_{44} \end{pmatrix} + \dots \tag{A.27}$$

The relation  $\hat{\mathbf{G}}^+ = \hat{\mathbf{G}}$ , used in Section 4, is clear by inspection if one recalls (3.15). The expressions (3.14) and (3.16) for  $L$ , and (4.7) for  $\hat{L}$ , follow from the definitions (3.9), (3.11), and (4.5) by substitution of the results obtained in this Appendix for  $M$ ,  $\mathbf{G}$ , and  $\hat{\mathbf{G}}$ , and inversion of the power series for  $\mathbf{G}$  and  $\hat{\mathbf{G}}$ .

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