

### Nonlinear Burnett coefficients

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We derive exact equilibrium fluctuation expressions for the nonlinear Burnett coefficients for the electrical conductivity of a fluid. The Burnett coefficients define a Taylor-series expansion of the conductivity in powers of the electrical current density. The fluctuation expressions may be calculated from an analysis of the time-dependent fluctuations of the equilibrium system constrained so that the mean electrical current is zero.

#### I. INTRODUCTION

We have recently derived fluctuation expressions for the derived properties of nonequilibrium steady states such as the thermal expansion coefficients and the specific heats.<sup>1,2</sup> The derivation of these expressions depended upon the development of a tractable nonlinear response theory.<sup>3</sup> Although other representations have been developed, there are two principal expressions for the thermostatic nonlinear response of an arbitrary phase variable,  $B(\Gamma)$ , to a perturbing external field  $F_e$ . If a canonical ensemble of systems  $f(0) = \exp[-\beta H_0(\Gamma)] / \int d\Gamma \exp[-\beta H_0(\Gamma)]$  is subject to the external field which is turned on at  $t=0$ , then the transient time correlation function expression for the thermostatic response at time  $t$  is<sup>3,4</sup>

$$\langle B(t_F) \rangle = \langle B(0) \rangle - \beta F_e \int_0^t ds \langle J(0)B(s_F) \rangle . \quad (1)$$

The dissipative flux  $J$  is defined in terms of the adiabatic (i.e., unthermostatic) derivative of the internal energy  $H_0$ ,

$$H_0 |^{ad} \equiv -J(\Gamma)F_e . \quad (2)$$

We use the notation  $B(t_F)$  to denote the phase variable  $B$  propagated in time with the field-dependent thermostatic phase propagator. In its adiabatic form Eq. (1) was first derived by Dufty and Lindenfeld<sup>5</sup> and later by Cohen.<sup>6</sup> Morriss and Evans were the first to give the thermostatic generalization.<sup>3</sup> They have also tested this generalization using nonequilibrium molecular dynamics computer simulation (NEMD), and found that the direct simulation agrees within statistical uncertainties, with the transient time correlation function (TTCF) prediction.<sup>4</sup>

A second but formally equivalent representation for the thermostatic nonlinear response has also been derived by Morriss and Evans,<sup>3</sup>

$$\langle B(t_F) \rangle = \frac{\left\langle B(0) \exp \left[ -\beta F_e \int_0^t ds J(-s_F) \right] \right\rangle}{\left\langle \exp \left[ -\beta F_e \int_0^t ds J(-s_F) \right] \right\rangle} . \quad (3)$$

This representation for the nonlinear response is called the Kawasaki representation since Kawasaki first derived

equations of this form in treating the adiabatic nonlinear response of systems to planar Couette flow.<sup>7</sup>

These expressions may be used as nonequilibrium partition functions. For example, if a particular derivative commutes with the thermostatic, field-dependent propagators implicit in (1) and (3), then one can formally differentiate both sides of these equations yielding fluctuation expressions for the so-called derived properties.<sup>1,2</sup> The key point in such derivations is that the particular derivative should commute with the relevant propagators. If this is not so, one cannot derive tractable or useful results.

In order to constrain thermodynamic variables two basic feedback mechanisms are employed: the integral feedback mechanism employed for example in the Nose-Hoover thermostat<sup>8</sup> and the differential mechanism employed in the Gaussian thermostat.<sup>9</sup> A third mechanism, the proportional mechanism, has not found much use in either simulations or in theory because it necessarily employs *irreversible* equations of motion.<sup>10</sup>

For our present purpose of differentiating expressions for phase averages with respect to the thermodynamic flux, we will use the Gaussian mechanism to fix the current at its initial value. We will then apply constant-current dynamics to an ensemble of initial phases whose currents are distributed normally about a prescribed value,  $J_0$ . Since the subsequent dynamics are independent of  $J_0$ , calculating the derivatives of steady-state averages with respect to  $J_0$  essentially involves differentiation of the initial distribution function. No terms arise from differentiation of the propagator.

In the present paper we will use these ideas to derive useful fluctuation expressions for the nonlinear Burnett coefficients.<sup>6</sup> These coefficients  $L_i$  give a Taylor-series representation of a nonlinear transport coefficient  $L(X)$  defined by a constitutive relation between a thermodynamic force  $X$  and a thermodynamic flux  $J(\Gamma)$ ,

$$\begin{aligned} \langle J \rangle &= L(X)X \\ &= L_1 X + \frac{1}{2!} L_2 X^2 + \frac{1}{3!} L_3 X^3 + \dots \end{aligned} \quad (4)$$

It is clear from this equation that the Burnett coefficients are given by the appropriate partial derivative of  $\langle J \rangle$ , evaluated at  $X=0$ . In this paper we will actually be

working in the Norton ensemble in which the thermodynamic force  $X$  is the dependent rather than the independent variable.<sup>11</sup> So we will in fact derive expressions for the inverse Burnett coefficients.

We will use two independent methods to show that the steady-state derivative of phase variables with respect to the current is simply related to the steady-state covariance of that phase variable and the current.

The formulas we derive in this paper are statistical rather than mechanical in nature. Response theory has often been criticized as being no more than mechanical perturbation theory.<sup>6,12</sup> This implies there is no direct connection between the linearity of individual trajectory responses and the ensemble averages of trajectory responses. The results derived in this paper do not require a detailed description of dynamics. They do, however, require a detailed specification of the ensembles used. The results derived are quite specific with regard to the ensemble employed.

## II. EQUATIONS OF MOTION

Consider the following equations of motion for an  $N$ -particle system of charged particles which describe the motion in a system with fixed current and fixed kinetic energy. For simplicity we assume that the system is electrically neutral and consists only of univalent ions of charge  $\pm e = \pm 1$ . This system is formally identical to the color conductivity system which has been subject to a number of studies,<sup>11,13,14</sup>

$$\dot{\mathbf{q}}_i = \frac{\dot{\mathbf{p}}_i}{m} \equiv \mathbf{v}_i, \quad (5)$$

$$m \dot{\mathbf{v}}_i = \mathbf{F}_i + i\lambda e_i - \alpha(\mathbf{v}_i - ie_i J). \quad (6)$$

The intermolecular forces are given by  $\mathbf{F}_i$ . In these equations,  $\lambda$  and  $\alpha$  are Gaussian multipliers chosen so that the  $x$  component of the current per particle,  $J = \sum_i e_i v_{xi} / N$ , and the temperature,  $T = \sum_i m (\mathbf{v}_i - ie_i J)^2 / 3Nk_B$ , are constants of the motion. This will be the case provided that

$$\lambda = - \frac{\sum_i F_{xi} e_i}{N} \quad (7)$$

and

$$\alpha = \frac{\sum_i \mathbf{F}_i \cdot (\mathbf{v}_i - ie_i J)}{\sum_i \mathbf{v}_i \cdot (\mathbf{v}_i - ie_i J)}. \quad (8)$$

In more physical terms  $\lambda$  can be thought of as an external electric field which takes on precisely those values required to ensure that the current  $J$  is constant. Because it precisely fixes the current, it is a phase variable. It is clear from (7) that the form of the phase variable  $\lambda$  is independent of the value of the current. Of course the ensemble average of  $\lambda$  will depend on the average value of the current. It is also clear that the expression for  $\alpha$  is similarly independent of the average value of the current.

These points can be clarified by considering an initial ensemble characterized by the canonical distribution

function,  $f(0)$ ,

$$f(0) = \frac{\exp \left[ -\beta \left[ \sum_i \frac{m}{2} (\mathbf{v}_i - e_i \mathbf{J}_0)^2 + \Phi \right] \right]}{\int d\Gamma \exp \left[ -\beta \left[ \sum_i \frac{m}{2} (\mathbf{v}_i - e_i \mathbf{J}_0)^2 + \Phi \right] \right]}. \quad (9)$$

In this equation  $\mathbf{J}_0$  is a constant which is equal to the canonical average of the current,

$$\langle \mathbf{J}(0) \rangle = \mathbf{J}_0 = iJ_0. \quad (10)$$

If we now subject this ensemble of systems, which we will refer to as the  $J$  ensemble, to the equations of motion (5) and (6), the electrical current and the temperature of each system will remain fixed at their initial values and the mean value of the field multiplier  $\lambda$  will be determined by the electrical conductivity of the system.

It is relatively straightforward to apply the theory of nonequilibrium steady states<sup>3</sup> to this system. It is easily seen from the equations of motion that the condition known as the adiabatic incompressibility of phase space holds.<sup>3</sup> Using Eq. (7), the adiabatic time derivative of the energy functional is easily seen to be

$$\dot{H} |^{\text{ad}} \equiv \frac{d}{dt} \Big|_{\text{ad}} \left[ \sum_i \frac{m}{2} (\mathbf{v}_i - e_i \mathbf{J}_0)^2 + \Phi \right] = N\lambda(\Gamma)J(\Gamma). \quad (11)$$

In this equation  $\Phi$  is the intermolecular potential energy. This equation is unusual in that the adiabatic derivative does not factorize into the product of a dissipative flux and the magnitude of a perturbing external field. This is because in the  $J$  ensemble the obvious external field  $\lambda$  is in fact a phase variable, and the current  $J$  is a constant of the motion. As we shall see this causes us no particular problems. The last equation that we need for the application of nonlinear response theory is the derivative,

$$\frac{\partial}{\partial \mathbf{J}_0} H = -mN(\mathbf{J} - \mathbf{J}_0). \quad (12)$$

## III. KAWASAKI REPRESENTATION

If we use the isothermal generalization of the Kawasaki expression for the average of an arbitrary phase variable  $B$ , we find

$$\langle B(t_J) \rangle = \frac{\left\langle B(0) \exp \left[ \beta N \int_0^{-t} ds J \lambda(s_J) \right] \right\rangle}{\left\langle \exp \left[ \beta N \int_0^{-t} ds J \lambda(s_J) \right] \right\rangle}. \quad (13)$$

In distinction to the usual case we have treated in the past,<sup>3</sup> the Kawasaki exponent involves a product of two phase variables  $J$  and  $\lambda$ , rather than the usual product of a dissipative flux (i.e., a phase variable), and a time-dependent external field. We use the suffix  $J$  on the time arguments to denote Gaussian thermostatic, constant current dynamics. The only place that the ensemble averaged current appears in (13) is in the initial ensembles

averages. We can therefore easily differentiate (13) with respect to  $J_0$  to find that

$$\begin{aligned} \frac{\partial \langle B(t_J) \rangle}{\partial J_0} &= \beta m N \langle \Delta B(t_J) \Delta J(0) \rangle \\ &= \beta m N \langle \Delta B(t_J) \Delta J(t_J) \rangle, \end{aligned} \quad (14)$$

where  $\Delta(B(t)) = B(t) - \langle B(t) \rangle$  and  $\Delta(J(t)) = J(t) - \langle J(t) \rangle = J(t) - J_0$ . This is an exact canonical ensemble expression for the  $J$  derivative of the average of an arbitrary phase variable. If we let  $t$  tend toward infinity we obtain a steady-state fluctuation formula which complements the ones we derived earlier for the temperature and pressure derivatives.

One can check that this expression is correct by rewriting the right-hand side of (14) as an integral of responses over a set of Norton ensembles in which the current takes on specific values. We shall call the subset of a  $J$  ensemble in which the current takes on a precisely fixed value a  $\Delta J$  ensemble. Using Eq. (9) we can write the average of  $B(t)$  as

$$\langle B(t) \rangle = \frac{\int dJ \exp(-\beta m N \Delta J^2 / 2) \langle B(t); J \rangle}{\int dJ \exp(-\beta m N \Delta J^2 / 2)}. \quad (15)$$

We use the notation  $\langle B(t); J \rangle$  to denote a  $\Delta J$  ensemble. The probability of the  $J$  ensemble taking on an initial  $x$  current of  $J$  is easily calculated from (9) to be proportional to  $\exp(-\beta m N \Delta J^2 / 2)$ . Since the current is a constant of the motion, we do not need to specify a time at which the current takes on the specified value.

Differentiating (15), we can write the derivative with respect to the average current as a superposition of  $\Delta J$ -ensemble contributions,

$$\begin{aligned} \frac{\partial \langle B(t) \rangle}{\partial J_0} &= \beta m N \frac{\int dJ \exp(-\beta m N \Delta J^2 / 2) \Delta J \langle B(t_J); J \rangle}{\int dJ \exp(-\beta m N \Delta J^2 / 2)} \\ &= \beta m N \langle \Delta B(t_J) \Delta J(0) \rangle. \end{aligned} \quad (16)$$

This expression is, of course, identical to Eq. (14) which was derived using the Kawasaki distribution. It was derived, however, without the use of perturbative mechanical considerations such as those implicit in the use of the Kawasaki distribution. This second derivation is based on two points: the initial distribution gives a normal distribution of currents about  $J_0$ , and the dynamics preserves the value of the current. Of course, the result is still valid even when  $J$  is not exactly conserved provided that the timescale over which it changes is much longer than the timescale for the decay of steady state fluctuations.

We will now derive relations between the  $J$  derivatives in the  $J$  ensemble and in the constrained ensemble in which  $J$  takes on a precisely fixed value (the  $\Delta J$  ensemble). In the thermodynamic limit the spread of possible values of  $\Delta J$  will become infinitely narrow suggesting that we can write a Taylor expansion of  $\langle B(t_J); J \rangle$  in powers of  $\Delta J$  about  $J_0$ :

$$\begin{aligned} \langle B(t_J); J \rangle &= \langle B(t_J); J_0 \rangle + \Delta J \frac{\partial \langle B(t_J); J_0 \rangle}{\partial J} \\ &\quad + \frac{\Delta J^2}{2!} \frac{\partial^2 \langle B(t_J); J_0 \rangle}{\partial J^2} + \dots \end{aligned} \quad (17)$$

Substituting (17) into (16) and performing the Gaussian integrals over  $J$ , we find that

$$\frac{\partial \langle B(t_J) \rangle}{\partial J_0} = \frac{\partial \langle B(t_J); J_0 \rangle}{\partial J} + \frac{1}{2\beta m N} \frac{\partial \langle B(t_J); J_0 \rangle}{\partial J^3} + \dots \quad (18)$$

This is a very interesting equation. It shows the relationship between the derivative computed in a canonical ensemble and a  $\Delta J$  ensemble. It shows that differences between the two ensembles arise from *nonlinearities* in the local variation of the phase variable with respect to the current. It is clear that these ensemble corrections are of order  $1/N$  compared to the leading terms.

#### IV. THE TTCF REPRESENTATION

If one differentiates and, in turn, reintegrates the Kawasaki expression (13), with respect to time one generates the so-called transient time correlation function representation for a nonequilibrium phase average:

$$\langle B(t_J) \rangle = \langle B(0) \rangle + \beta N \int_0^t ds \langle \Delta B(s_J) \lambda(0) J \rangle. \quad (19)$$

The initial values of the current will be clustered about  $J_0$ . If we write

$$\langle \Delta B(s) \lambda(0) J \rangle = \langle \Delta B(s) \lambda(0) \rangle J_0 + \langle \Delta B(s) \lambda(0) \Delta J \rangle, \quad (20)$$

it is easy to see that if  $B$  is extensive then the two terms on the right-hand side of (20) are  $O(1)$  and  $O(1/N)$  respectively. For large systems we can therefore write

$$\langle B(t) \rangle = \langle B(0) \rangle + \beta N \int_0^t ds \langle \Delta B(s_J) \lambda(0) \rangle J_0. \quad (21)$$

It is now a simple matter to calculate the appropriate  $J$  derivatives:

$$\begin{aligned} \frac{\partial \langle B(t_J) \rangle}{\partial J_0} &= \beta N \int_0^t ds \langle B(s_J) \lambda(0) \rangle \\ &\quad + \beta J_0 N \int_0^t ds \int d\Gamma B(s_J) \lambda(0) \frac{\partial f(0)}{\partial J_0} \\ &= \beta N \int_0^t ds \langle B(s_J) \lambda(0) \rangle \\ &\quad + \beta^2 J_0 m N^2 \int_0^t ds \langle B(s_J) \lambda(0) \Delta J \rangle. \end{aligned} \quad (22)$$

This equation relates the  $J$  derivative of phase variables to transient time correlation functions. If we apply these formulas to the calculation of the leading Burnett coefficient we, of course, evaluate the derivatives at  $J_0 = 0$ . In this case the TTCF's become equilibrium time correlation functions. The results for the leading Burnett coefficients are

$$\left. \frac{\partial \langle B(t_J) \rangle}{\partial J_0} \right|_{J_0=0} = \beta N \int_0^t ds \langle B(s_J) \lambda(0) \rangle_{\text{eq}}, \quad (23)$$

$$\left. \frac{\partial^2 \langle B(t_J) \rangle}{\partial J_0^2} \right|_{J_0=0} = 2\beta^2 m N^2 \int_0^t ds \langle B(s_J) \lambda(0) \Delta J \rangle_{\text{eq}}, \quad (24)$$

$$\left. \frac{\partial^3 \langle B(t_J) \rangle}{\partial J_0^3} \right|_{J_0=0} = 3\beta^3 m^2 N^3 \int_0^t ds \langle B(s_J) \lambda(0) \times (\Delta^2 J - \langle \Delta^2 J \rangle) \rangle_{\text{eq}}. \quad (25)$$

Surprisingly, the expressions for the Burnett coefficients only involve equilibrium, two-time correlation functions. At long times assuming that the system exhibits mixing they break each factor into a triple product  $\langle B(s \rightarrow \infty) \rangle \langle \lambda(0) \rangle \langle \text{cumulants}(J) \rangle$ . The terms involving  $\lambda(0)$  and the cumulants of  $J(0)$  factor, because at

time zero the distribution function is (9), factor into kinetic and configurational parts. Of course, these results for the Burnett coefficients could have been derived from the transient time correlation function (19), using the  $\Delta J$  ensemble methods used earlier.

## V. DISCUSSION

We have derived a number of new results for the nonlinear dynamic susceptibilities of nonequilibrium steady states. The derivations are statistical rather than perturbative in nature, and hence they avoid many of the earlier criticisms of response theory. Equation (14) shows that the dynamic susceptibility has a simple relation to steady-state fluctuations. It is essentially identical in form to that found earlier for the compressibility of steady states.<sup>2</sup>

The results for the Burnett coefficients are particularly simple in form, and it is hoped that they may find use in computer simulation studies of nonequilibrium systems.

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