Efficient determination of the nonlinear Burnett coefficients

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In a previous paper [R. K. Standish and D. J. Evans, Phys. Rev. A **41**, 4501 (1990)], simple equilibrium expressions were obtained for the nonlinear Burnett coefficients. In this paper, we devise a more efficient way of using these expressions and show some preliminary results from a color-conductivity simulation.

I. INTRODUCTION

Ever since the Green-Kubo formalism for calculating the linear transport coefficients was developed, there has been interest in a corresponding theory for the nonlinear Burnett coefficients. The discovery of long-time tails in the velocity autocorrelation function by Alder and Wainwright [1] indicated that the hydrodynamic transport coefficients do not exist in two dimensions, but do exist in three dimensions. By applying mode-coupling theories, Ernst *et al.* [2] showed that the relation between stress and strain rate should be $P_{xy} \propto |\gamma| \ln |\gamma|$ for hard disks and $P_{xy} = -\eta\gamma + c|\gamma|^{\frac{3}{2}}$ for hard spheres, which are nonanalytic constitutive relations. These results indicate that the nonlinear Burnett coefficients do not exist at all, so the interest has intensified for a numerical simulation to test the mode-coupling theories.

In a recent paper by Evans and Lynden-Bell [3], equilibrium fluctuation expressions for inverse Burnett coefficients were derived for the color-conductivity problem. The coefficients B_i give a Taylor series representation of a nonlinear transport coefficient L, in terms of the thermodynamic force F. Thus if a thermodynamic flux J is written in terms of the coefficient's defining constitutive relation as $\langle J \rangle = L(F)F$, then the Burnett coefficients are related by $L(F) = B_0 + B_1 F + B_2 F^2 + \cdots$. In order to derive closed form expressions for the Burnett coefficients, it was found necessary to work in the Norton ensemble, in which the flux J rather than the thermodynamic force F was the independent variable. The constitutive relation in this case is $\langle F \rangle = \mathcal{L}(J)J = \mathcal{B}_0 + \mathcal{B}_1 J + \cdots$. In the thermodynamic limit, we may write $\mathcal{L}(J) = L^{-1}(J)$, and so the nonlinear Burnett coefficients can be computed by inverting the series.

Evans and Lynden-Bell [3] applied constant current dynamics to a canonical ensemble with the currents distributed about an average current J_0. This allowed the derivation of a transient time correlation function for the nonequilibrium phase average $\langle F \rangle$. It was then a simple matter to compute the derivatives of $\langle F \rangle$ with respect to the average current J_0, as the constant current propagator commutes with the derivative operator. However, this method appeared to be limited to color currents for which an appropriate canonical distribution could be found. In a previous paper [4] we show that this method can be applied to the situation of an arbitrary thermodynamic flux. In this paper we show that the transient time correlation expression derived in the previous paper can be expressed in terms of an average over an equilibrium simulation, reducing the calculation required by two orders of magnitude. Further, we shall report on results recently obtained which show that such simulations are just within the capability of computers available now.

In order to avoid confusion, it should be noted that the term "color diffusion" is sometimes used in the sense of the diffusion of color labels attached to otherwise color-blind particles in the complete absence of applied external fields [5]. In this approach if the color label attached to a particle is ignored, the system remains at equilibrium. This is manifestly a linear process. In the model we consider all the particles interact with an external color sensitive external field and this allows the possibility of a nonlinear response. It might also be pointed out the the color field we consider here is independent of both position and time so that the *linear* Burnett coefficients do not play a role.

II. EQUILIBRIUM SIMULATION

Recall that transient time correlation functions for evaluating the first three derivatives of a phase space variable B with respect to a nonequilibrium flux $J_0 = \langle J \rangle$ about the equilibrium point $J_0 = 0$ are given in Ref. [4]:

$$\left. \frac{\partial \langle B(t_J) \rangle}{\partial J_0} \right|_{J_0=0} = \frac{\langle B(0)\Delta J \rangle}{\langle \Delta J^2 \rangle} + \beta N \int_0^t \langle B(s_J)\lambda(0) \rangle ds, \tag{1}$$

$$\frac{\partial^2 \langle B(t_J)\rangle}{\partial J_0^2}\bigg|_{J_0=0} = \frac{\langle B(0)(\Delta J^2 - \langle \Delta J^2\rangle)\rangle}{\langle \Delta J^2\rangle^2} - \frac{\langle B(0)\Delta J\rangle\langle\Delta J^3\rangle}{\langle\Delta J^2\rangle^3}$$
$$+ \frac{2\beta N}{\langle\Delta J^2\rangle}\int_0^t \langle B(s_J)\lambda(0)\Delta J\rangle ds, \tag{2}$$

$$\frac{\partial^3 \langle B(t_J)\rangle}{\partial J_0^3}\bigg|_{J_0=0} = \frac{\langle B(0)\Delta J^3\rangle}{\langle\Delta J^2\rangle^3} - \frac{3\langle\Delta J^3\rangle}{\langle\Delta J^2\rangle^4}\langle B(0)\Delta J^2\rangle$$
$$+ \left(\frac{3\langle\Delta J^3\rangle^2}{\langle\Delta J^2\rangle^5} - \frac{\langle\Delta J^4\rangle}{\langle\Delta J^2\rangle^4}\right)\langle B(0)\Delta J\rangle + \frac{2\langle\Delta J^3\rangle}{\langle\Delta J^2\rangle^3}\langle B(0)\rangle$$
$$- \frac{3N\beta\langle\Delta J^3\rangle}{\langle\Delta J^2\rangle^3}\int_0^t \langle B(s_J)\lambda(0)\Delta J\rangle ds$$
$$+ \frac{3N\beta}{\langle\Delta J^2\rangle^2}\int_0^t \langle B(s_J)\lambda(0)(\Delta J^2 - \langle\Delta J^2\rangle)\rangle ds, \tag{3}$$

where λ is a phase variable conjugate to J that serves to keep the simulation at constant flux, and the phase average is taken over a canonical ensemble $f_0 = \exp(-\beta H)/\int \exp(-\beta H)d\Gamma$. These same equations are valid if the flux-controlling and thermostating mechanisms used are Nosé-Hoover rather than the Gaussian mechanism used in Ref. [4]:

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{C}_i\lambda,$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i\lambda - \alpha\mathbf{p}_i,$$
$$\dot{\alpha} = \frac{3Nk_B}{Q_\alpha}(T - T_0),$$
$$\dot{\lambda} = \frac{N}{Q_\lambda}[J - J(t=0)], \tag{4}$$

where $\mathbf{F}_i$ are the intermolecular forces, $T = \sum_i \frac{mp_i^2}{3Nk_B}$, and $T_0 = \langle T\rangle$. It should be noted that the operation of differentiation with respect to J_0 commutes with the propagator arising from Eq. (4), a fact that is used in the derivation of expressions (1)–(3).

When the flux is fixed in this manner, the ensemble is termed a Norton ensemble. When the thermodynamic force is fixed, then it is termed a Thévenin ensemble by analogy with electrical circuits [6]. We have recently given a statistical mechanical proof of the macroscopic equivalence of the Norton and Thévenin representations of a nonequilibrium system [7]. As discussed in Ref. [4], these equations are quite general. For specificity, consider the color current model discussed in the previous references. In this case, $\mathbf{C}_i = 0$ and $\mathbf{D}_i = e_i\hat{\mathbf{x}}$, where e_i is the color charge of molecule i. Half of the molecules have positive charge ($e_i = +1$) and the other have negative charge ($e_i = -1$). The feedback parameter λ can be identified with the amount of external force required to fix the current at a particular level.

The two time correlation functions in Eqs. (1)–(3) are averaged over an ensemble of flux-controlled trajectories. To calculate this, one would first need to generate the distribution f_0, using molecular dynamics simulation or Monte Carlo methods. If generated by molecular dynamics, then a trajectory of an equilibrium system is sampled to form the ensemble of initial states. Obviously, the sampling time should be comparable with the mixing or correlation time of the system. Once an initial phase space configuration Γ_0 was produced with probability $f_0(\Gamma_0)$, then its evolution under the flux-controlled equations of motion needs to be followed. If we wish to follow these trajectories for n_t sample times, then we require $n_\Gamma n_t$ sample times to average over n_Γ trajectories. By contrast, the Green-Kubo expressions for the linear transport coefficients involve correlation functions whose propagator is independent of the initial state of the trajectory. We can therefore form the average as

$$\langle A(t)B(0)\rangle = \frac{1}{n_\Gamma}\sum_{j=1}^{n_\Gamma} A(t + j\tau)B(j\tau),$$

with τ being the time step. This clearly requires only $n_\Gamma + n_t$ sample times, and so it is more efficient by a factor of $\frac{n_\Gamma n_t}{n_\Gamma + n_t}$, provided that the time required to generate a new ensemble member (τ) can be neglected with respect to the required time to follow the trajectories. We shall see in this section that the ensemble averages in Eqs. (1)–(3) can be calculated from a single equilibrium trajectory, with the consequent improvement in efficiency. Write the flux-controlled propagator explicitly as $e^{iL_J t}$, where $\mathcal{J}$ is enscripted to indicate that it is not a phase variable:

$$\langle A(0)B(t_J)\rangle = \int f_0(\mathcal{J})\langle Ae^{iL_J t}B;\mathcal{J}\rangle d\mathcal{J}. \tag{5}$$

This explicitly shows that an ensemble of propagators is used in expressions (1)–(3). We will now show that this ensemble may be replaced by an ensemble having a single propagator statted to the mean flux J_0.

The Dyson equation [8] may be used to expand $e^{iL_J t}$ in terms of $e^{iL_{J_0} t}$:

$$\langle Ae^{iL_J t}B;\mathcal{J}\rangle = \langle Ae^{iL_{J_0} t}B;\mathcal{J}\rangle$$
$$+ \left\langle A\int_0^t e^{iL_J(t-s)}i\Delta Le^{iL_{J_0} s}Bds;\mathcal{J}\right\rangle$$
$$+ \cdots. \tag{6}$$

For $L_{\mathcal{J}}$ being the flux-controlled Liouvillean with Nosé-Hoover feedback mechanism, the difference in operators is contained only in the equation of motion for λ:

$$i\Delta L = \Delta\dot{\lambda}\partial_\lambda = \frac{N}{Q_\lambda}(\mathcal{J} - J_0)\partial_\lambda.$$

Since $\mathcal{J} - J_0$ is not a phase variable, it commutes with $L_{\mathcal{J}}$. Defining $B' \equiv \int_0^t e^{iL_{\mathcal{J}}(t-s)}\partial_\lambda e^{iL_{J_0}s}B\,ds$, we may write the series (6) as

$$\langle B(t_{\mathcal{J}})A(0); \mathcal{J}\rangle = \langle B(t_{J_0})A(0); \mathcal{J}\rangle$$
$$+\langle B'A(\mathcal{J} - J_0); \mathcal{J}\rangle + \cdots.$$

Substituting this into (5) reveals

$$\langle B(t_J)A(0)\rangle = \langle B(t_{J_0})A(0)\rangle + \langle B'A\Delta J\rangle + \cdots. \quad (7)$$

As B' is intensive, the result given in the Appendix shows that the higher terms will vanish in the thermodynamic limit, provided that $B(t_{\mathcal{J}})$ vanishes in mean for all $\mathcal{J}$, or it never has zero mean for any $\mathcal{J}$. This is clearly true of $\lambda(s_{\mathcal{J}})$ for both the color-conductivity model and the planar couette flow model; it vanishes in mean for symmetry reasons. In the thermodynamic limit, Eq. (7) becomes

$$\langle B(t_J)A(0)\rangle = \langle B(t_{J_0})A(0)\rangle. \quad (8)$$

Thus the time correlation functions of (1)–(3) are expressed in terms of an average over a single trajectory, provided that the flux-controlling propagator generates f_0. This is the case for the Nosé-Hoover feedback mechanism discussed, when $J_0 = 0$.

III. NUMERICAL EVALUATION OF BURNETT COEFFICIENTS

In order to establish the feasibility of calculations based on Eq. (3), it was decided to perform a calculation using the color-conductivity model described in Evans and Lynden-Bell [3]. The intermolecular potential was taken to be the Lennard-Jones potential, which has an attractive component due to van der Waals interaction and a repulsive hard core that goes as r^{-12}:

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right].$$

In what follows, every quantity will be given in reduced units, in which $\varepsilon = \sigma = m = 1$. This model has been well studied and can be related physically to some noble gases such as argon. The correlations between different successive states of the equilibrium simulation can be easily seen by examining something such as the velocity autocorrelation function (see Fig. 7.1 of [9] for examples). The correlation time for this system is about 1.

The system consists of 32 (or 108) particles at a temperature of 1.08 and density of 0.85. This state point was chosen because considerable information was already known about this system at that state point [6].

The equations of motion employed were the Nosé-

Hoover feedback mechanism for the Norton ensemble [Eq. (4)] with $J = \sum_i \frac{p_{xi}e_i}{Nm}$, $\mathbf{C}_i = \mathbf{0}$, and $\mathbf{D}_i = e_i\hat{\mathbf{x}}$, where e_i is the charge on the ith molecule. In accordance with the previous discussion, the simulation is performed at equilibrium $[J(t = 0) = 0]$. The feedback parameter Q_λ was chosen to be of order unity and Q_α to be 0.96. The values of these parameters were chosen to give optimal convergence of the linear response function. There is no real reason for them to be optimal for nonlinear response functions.

Initially, a 108 particle system was simulated on a Fujitsu VP100 supercomputer. The code executed 1.2×10^6 time steps per hour, or about 75 Mflops. Even after 200 hours of CPU time, the statistics were still poor, although a nonlinear response could be seen. Later on, Sun SPARCstation computers became available, which could be used as nodes of a Multiple Instruction, Multiple Data computer (MIMD), each running a copy of the system. The phase averages could now be taken over the ensemble of systems, as well as time. The network of approximately 30 workstations had about the same speed as the VP100 for a 108 particle system, and about half the speed for the 32 particle system (6 million time steps an hour versus 12 million on the VP100). However, as the workstation network was not being used for any other CPU intensive purpose, it represented an 8 to 16 times throughput over the VP100 supercomputer. The work reported here represents accumulation of data for 1.2×10^{10} time steps of a 32 particle system. Figure 1 shows $\frac{\partial^3\langle\lambda(t)\rangle}{\partial J^3}$ for the system under study for $Q_\lambda = 2$. As mentioned before, the units employed are the reduced units for the Lennard-Jones system, in which (for example) time is measured in units of $\tau = \sigma\sqrt{m/\varepsilon}$. Figure 2 shows the time derivative of this function. The long (negative) tail shown in this figure lies within two standard deviations of zero, the error bar showing the size of the noise. Clearly, another order of magnitude of computer power is required to resolve the issue of whether this is a long time tail or not.

In terms of efficiency relative to the method proposed in [4], the sample time should be about 1 (corresponding to the correlation time), so $n_t \approx 2$. Therefore the present method is efficient by a factor of $n_\Gamma\frac{2}{1+2/n_\Gamma}$, i.e.,
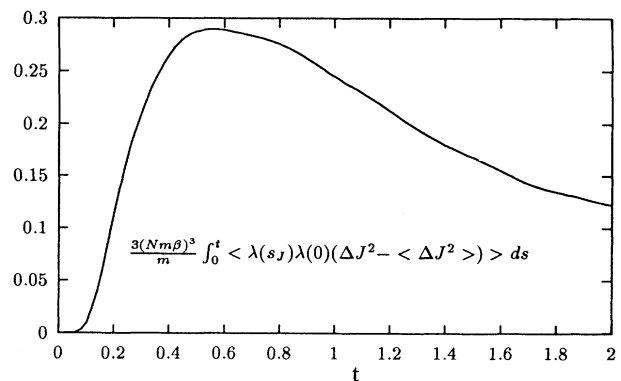

FIG. 1. The third-order response $\partial^3\langle\lambda(t)\rangle/\partial J_0^3$. Only the last term on the right-hand side of (3) is nonzero for this case.
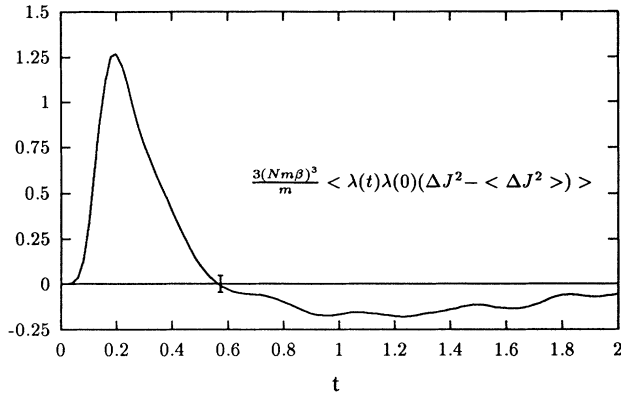
FIG. 2. The time derivative of the response shown in Fig. 1.

about twice as efficient in the long term (as $n_\Gamma \longrightarrow \infty$). In fact the efficiency improvement is probably a bit better than this, because the present method allows sampling at smaller than the correlation time at virtually no extra cost, and even partially decorrelated states do contribute information to the final average. The calculations reported in this paper used a sample time of 1×10^{-2}.

IV. CONCLUSION

Phase space averages over equilibrium simulations offer a way of calculating nonlinear Burnett coefficients in much the same way as the Green-Kubo formula relates linear transport coefficients to equilibrium averages. This paper expands on earlier work in reporting an improved algorithm over previous papers [3,4] and reporting some preliminary results of simulations that show these calculations to be within the range of computer facilities available now.

It has been suggested [10] that the coefficients may diverge in the thermodynamic limit. To test this hypothesis requires running the simulation at different system sizes. At present, a 108 particle simulation is being run.

APPENDIX: SYSTEM SIZE DEPENDENCE OF A PRODUCT OF INTENSIVE PHASE VARIABLES

In this appendix, we show that the phase average of a product of zero mean intensive phase variables $\prod_{i=1}^{n} A_i$ is of order N^{1-n}, with N being the number of particles in the system.

Let us begin by noting that the phase variable A_i can be written as an average over individual particles:

$$A_i = \frac{1}{N} \sum_{j=1}^{N} A_{ij}.$$

Then we find that

$$
\left\langle \prod_{i=1}^{n} A_i \right\rangle = \frac{1}{N^n} \left\langle \prod_{i=1}^{n} \sum_{j=1}^{N} A_{ij} \right\rangle
$$

$$
= \frac{1}{N^n} \sum_{j=1}^{N} \left\langle \prod_{i=1}^{n} A_{ij} \right\rangle + \frac{1}{N^n} \sum_{i=1}^{N} \sum_{j(\neq i)} \sum_{k=2}^{n} \left\langle A_{1i} A_{kj} \left(\prod_{l=2}^{k-1} A_{li} \right) \left(\prod_{l=k+1}^{n} \sum_{m=1}^{N} A_{lm} \right) \right\rangle. \tag{A1}
$$

In a system where the order is short range (for example, a fluid far from its critical point), we would expect that correlations of the form $\sum_{i=1}^{N} \sum_{j(\neq i)} \langle A_{li} A_{kj} \cdots \rangle$ only pick up contributions from its near neighbors and are consequently intensive. However, $\sum_{j=1}^{N} \langle \prod_{i=1}^{n} A_{ij} \rangle$ is clearly extensive, so we find that

$$
\left\langle \prod_{i=1}^{n} A_i \right\rangle = O(N^{1-n}).
$$

If the any of the phase variables have nonzero mean, then we may use the binomial theorem to express the result in terms of a product of means. For example, if all variables have nonzero mean, we may write

$$
\left\langle \prod_{i=1}^{n} A_i \right\rangle = \sum_{j=0}^{n} \binom{n}{j} \left\langle \prod_{i=1}^{j} \Delta A_i \right\rangle \prod_{i=j+1}^{n} \langle A_i \rangle
$$

$$
= \prod_{i=1}^{n} \langle A_i \rangle + O(N^{-1}).
$$

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