Numerical evidence for divergent Burnett coefficients

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In previous papers [Phys. Rev. A **41**, 4501 (1990); Phys. Rev. E **18**, 3178 (1993)], simple equilibrium expressions were obtained for nonlinear Burnett coefficients. A preliminary calculation of a 32-particle Lennard-Jones fluid was presented in the previous papers. Now, sufficient resources have become available to address the question of whether nonlinear Burnett coefficients are finite for soft spheres. The hard sphere case is known to have infinite nonlinear Burnett coefficients (i.e., a nonanalytic constitutive relation) from mode-coupling theory. This paper reports a molecular dynamics caclulation of the third order nonlinear Burnett coefficient of a Lennard-Jones fluid undergoing color flow, which indicates that this term diverges in the thermodynamic limit. [S1063-651X(99)00511-5]

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I. INTRODUCTION

Ever since the Green-Kubo formalism for calculating 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 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 $P_{xy} = -\eta\gamma + c|\gamma|^{3/2}$ for hard spheres, which are nonanalytic constitutive relations. Similar results were obtained by Kawasaki and Gunton [3] for incompressible fluids (which is a particular case of a hard sphere fluid), although criticized later by Brey *et al.* [4]. It should be pointed out that the linear Burnett coefficients are known to be divergent [5,6], and, in light of the linear coefficient results, it is generally assumed that the nonlinear coefficients should be divergent as well for soft particle systems. Brey *et al.* [4] claimed to show the divergence of nonlinear coefficients in a followup paper (Ref. [11] in that paper), yet this paper never appeared in the literature. Therefore, there is considerable interest in a molecular dynamics simulation of a soft particle system to see if the hard sphere results generalize.

In a paper by Evans and Lynden-Bell [7], 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 $L(F) = B_0 + B_1F + B_2F^2 + \cdots$. 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 $\langle F\rangle = \mathcal{L}(J)J = \mathcal{B}_0 + \mathcal{B}_1J + \cdots$. 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 [7] 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 [8] we show that this method can be applied to the situation of an arbitrary thermodynamic flux. Later [9], we showed that this transient time correlation expression can be expressed in terms of an average over an equilibrium simulation, reducing the calculation required by two orders of magnitude. At the time, computational resources were not sufficient to establish whether this expression is finite in the limit as $t\to\infty$, or in the thermodynamic limit. In this paper, we present computational results of color conductivity in a Lennard-Jones system, harnessing four supercomputers simultaneously over a period of 18 months that show distinct evidence that $\mathcal{B}_2 = \infty$.

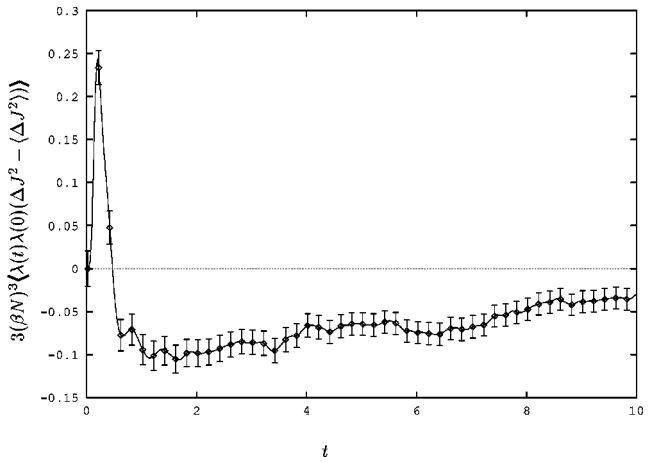

FIG. 1. Transient time correlation function for the 32-particle system with $Q_\lambda = 4.74$ at 1.32×10^{11} time steps.

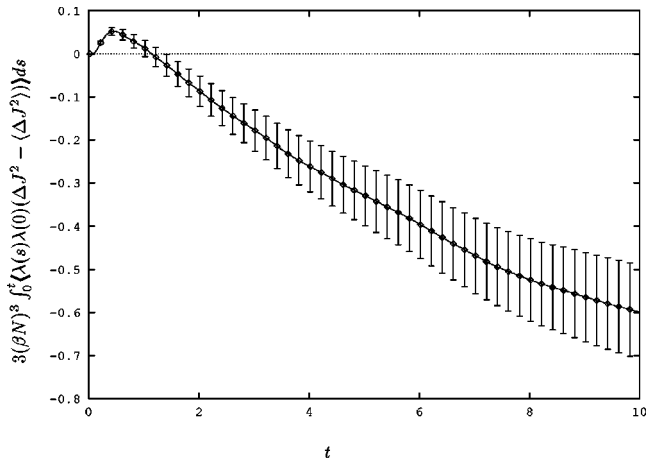

FIG. 2. Integral of the TTCF for the 32-particle system with $Q_\lambda = 4.74$ at 1.32×10^{11} time steps.

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 [10]. 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 that 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. SIMULATION

The simulation was performed using the color conductivity model described in Evans and Lynden-Bell [7]. 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}:

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

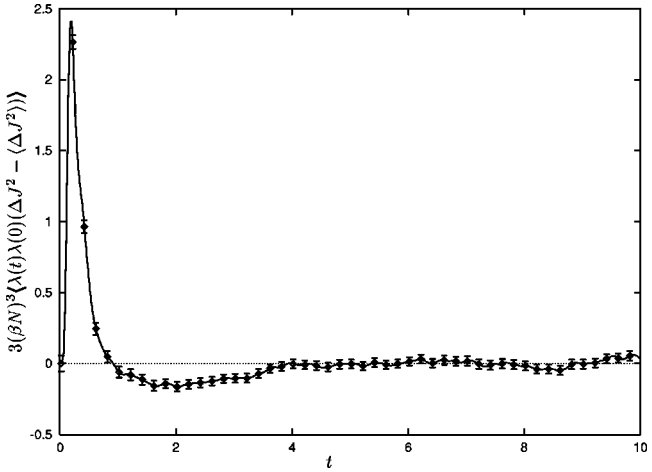

FIG. 3. Transient time correlation function for the 32-particle system with $Q_\lambda = 1.4$ at 2.2×10^{11} time steps.

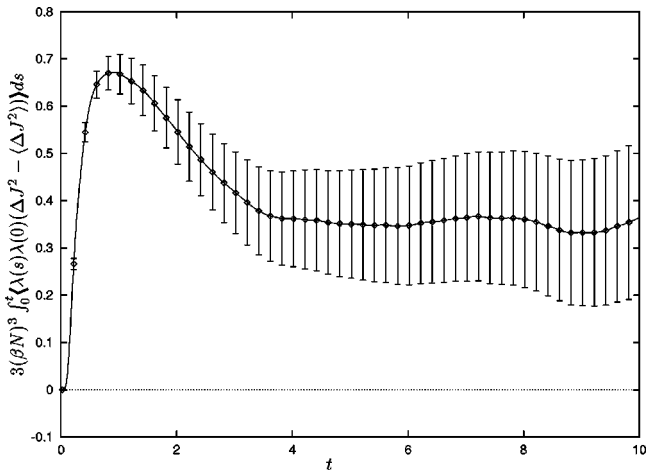

FIG. 4. Integral of the TTCF for the 32-particle system with $Q_\lambda = 1.4$ at 2.2×10^{11} time steps.

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 like argon.

The system was simulated at three different system sizes (32, 108, and 256 particles) using a periodic boundary condition to minimize boundary effects. The state point chosen had a temperature of 1.08 and density of 0.85. Considerable information was already known about this system at that state point [11].

The equations of motion are just that of the Nosé-Hoover thermostat, with an additional flux stating term. This generates a canonical ensemble

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m},$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + e_i \hat{\mathbf{x}} \lambda - \alpha \mathbf{p}_i,$$

$$\dot{\alpha} = \frac{3Nk_B}{Q_\alpha}(T - T_0),$$

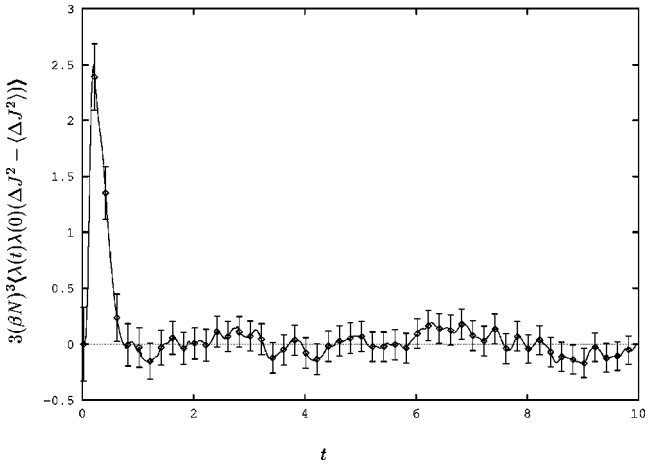

FIG. 5. Transient time correlation function for the 108-particle system at 1.1×10^{11} time steps.

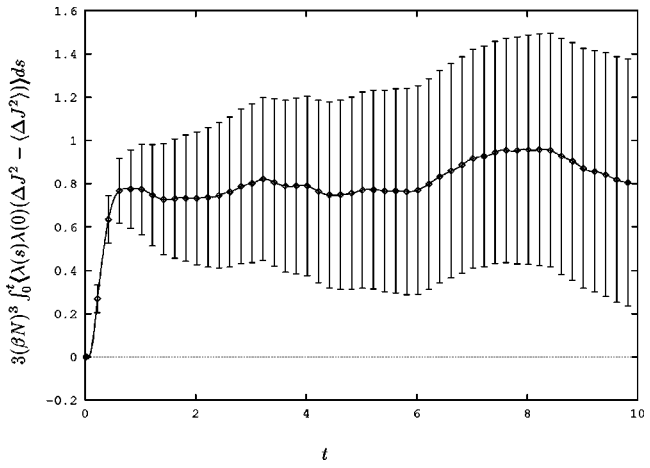

FIG. 6. Integral of the TTCF for the 108-particle system at 1.1×10^{11} time steps.

$$\dot{\lambda} = \frac{N}{Q_\lambda}[J - J(t=0)], \tag{1}$$

where $\mathbf{F}_i$ are the intermolecular forces, $e_i = \pm 1$ are the color charges, $T = \Sigma(mp_i^2/3Nk_B)$, $T_0 = \langle T \rangle$, and $J = \Sigma_i(p_{xi}e_i/Nm)$ is the color current.

The feedback parameter Q_λ was chosen equal to 4.74 for the 108-, the 256-, and one of the 32-particle runs. Because Q_λ should be an extensive quantity, the 32-particle run was repeated at $Q_\lambda = 32 \times 4.74/108 = 1.4$. The Nosé-Hoover thermostat parameter Q_α was chosen to be $0.31N$. 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.

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 [11]. Evons has recently given a statistical mechanical proof of the macroscopic equivalence of the Norton-Thévenin representations of a nonequilibrium system [12].

Recall that transient time correlation functions (TTCFs) for evaluating the inverse cubic Burnett coefficient $\mathcal{B}_2$ were given in Ref. [7]:

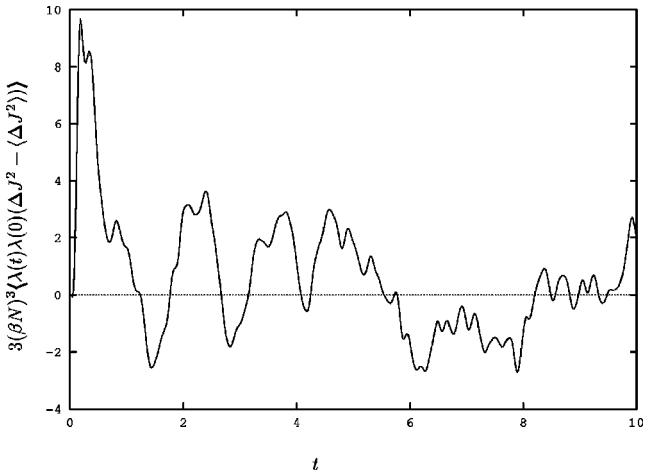

FIG. 7. Transient time correlation function for the 256-particle system at 3×10^{10} time steps.

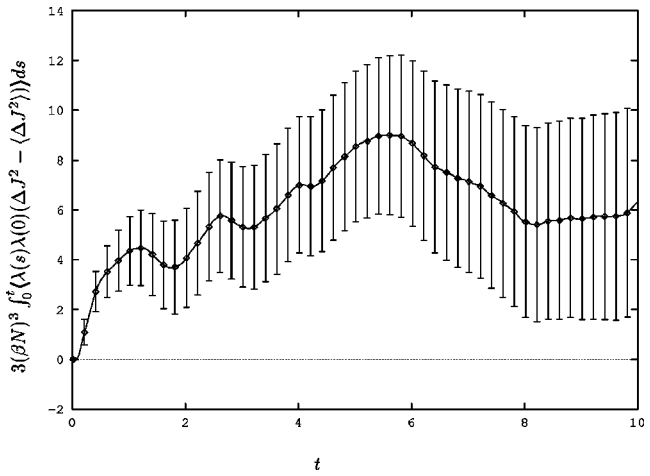

FIG. 8. Integral of the TTCF for the 256-particle system at 3×10^{10} time steps.

$$\mathcal{B}_2 = \frac{3N\beta}{\langle \Delta J^2 \rangle^2} \int_0^\infty \langle \lambda(s)\lambda(0)(\Delta J^2 - \langle \Delta J^2 \rangle)\rangle ds, \tag{2}$$

where $\lambda(s)$ is the additional phase variable [defined in Eq. (1) corresponding to a color force of a system at time s along a trajectory], and $\Delta J = J - J_0$ where J_0 is the color current at the origin of that trajectory. As the system is at equilibrium (in the canonical ensemble), after a correlation time has passed, the system's configuration is effectively randomized, and may be used as a new trajectory origin. The correlations between different successive states of the equilibrium simulation can be easily seen by examining something like the velocity autocorrelation function (see Fig 7.1 of Ref. [13], for examples). The correlation time for this system is about 1.

III. RESULTS

Because the relevant quantity is an ensemble average, a very effective parallelization strategy is to run a separate copy of the system on each processor, compute the TTCF on each processor, then average over the entire set of processors, weighing for the number of time steps executed on each processor. Further computational details of this experiment

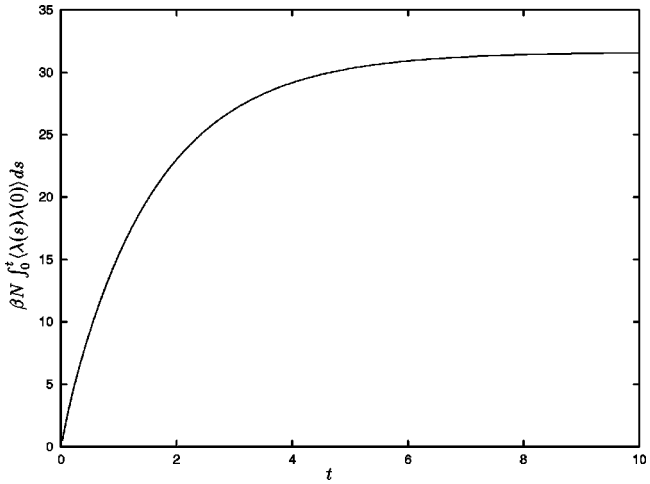

FIG. 9. Integral of the TTCF for the linear transport coefficient.

were reported in Ref. [14]. While the results of this experiment would appear meager compared with the computational resources used to compute it, it should be pointed out that this computation was conducted at the lowest priority on these machines, using idle CPU cycles.

Having a set of approximations also allows one to calculate the standard error of the TTCF. These are shown as error bars in Figs. 1–8.

The TTCF's and their integrals are shown in Figs. 1–8. There is a considerable system size dependence, indicating that the nonlinear Burnett coefficients diverge in the thermodynamic limit, although the individual TTCFs remain finite. It can be shown, using the lemma proved in the Appendix of Ref. [9], that the inverse nonlinear Burnett coefficients given by Eq. (2) should be intensive. As well as this, the 32 particle simulation shows strong evidence of a long time tail (Fig 1 and 2) when Q_λ is increased (softening the current-statting), leading to a divergence in the integrals as $t \to \infty$. For comparison, the transient time correlation function for the linear coefficient is shown in Fig. 9, showing convergence within $t=5$.

IV. CONCLUSION

This work presents strong numerical evidence in favor of infinite nonlinear Burnett coefficients for soft spheres as is the case for hard spheres. However, the Taylor series expansion of the constitutive relation presented in Ref. [8] can also be derived for $J_0 \neq 0$, which, if the hard sphere model is anything to go by, should be finite. These can be used to compute the constitutive relation into the nonlinear region. However, it will probably be at least another decade before these calculations become practical.

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