Numerical Evidence for Divergent Burnett Coefficients

Russell K. Standish

High Performance Computing Support Unit
The University of New South Wales

Abstract

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 paper. 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 (ie a nonanalytic constitutive relation) from mode coupling theory. This paper reports a molecular dynamics calculation of the third order nonlinear Burnett coefficient of a Lennard-Jones fluid undergoing colour flow, which indicates that this term is diverges in the thermodynamic limit.

05.20.-y,05.60.+w
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 non-analytic 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 criticised 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] claim 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 generalise.

In a paper by Evans and Lynden-Bell [7], equilibrium fluctuation expressions for inverse Burnett coefficients were derived for the colour 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 $\langle F \rangle = \mathcal{L}(J)J = B_0 + B_1 J + \cdots$. In the thermodynamic limit, we may write $\mathcal{L}(J) = L^{-1}(J)$, and so the non-linear 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 non-equilibrium 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 colour 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 colour conductivity in a Lennard-Jones system, harnessing 4 supercomputers simultaneously over a period of 18 months, that show distinct evidence that $B_2 = \infty$.

In order to avoid confusion, it should be noted that the term “colour diffusion” is sometimes used in the sense of the diffusion of colour labels attached to otherwise colour blind
particles in the complete absence of applied external fields [10]. In this approach if the colour 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 colour sensitive external field and this allows the possibility of a nonlinear response. It might also be pointed out that the colour field we consider here is independent of both position and time so that the linear Burnett coefficients do not play a role.

II. THE SIMULATION

The simulation was performed using the colour 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 $r^{-12}$:

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

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 3 different system sizes (32, 108 and 256 particles) using a periodic boundary condition to minimise 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 statting term. This generates a canonical ensemble:

$$\dot{q}_i = \frac{p_i}{m},$$

$$\dot{p}_i = F_i + e_i \dot{\lambda} - \alpha p_i,$$

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

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

where $F_i$ are the intermolecular forces, $e_i = \pm 1$ are the colour charges, $T = \sum \frac{m p_i^2}{2Nk_B}$, $T_0 = \langle T \rangle$ and $J = \sum_i e_i \dot{p}_i$ is the colour current.

The feedback parameter $Q_\lambda$ was chosen equal to 4.74 for the 108, 256 and one of the 32 particle runs. Because $Q_\lambda$ 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 $Q_\alpha$ 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 non-linear 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]. We have recently given a statistical mechanical proof of the macroscopic equivalence of the Norton and Thévenin representations of a nonequilibrium system [12].

Recall that Transient Time Correlation Functions for evaluating the inverse cubic Burnett coefficient $B_2$ is given in Ref. [7]:

$$B_2 = \frac{3N\beta}{\langle J^2 \rangle^2} \int_0^\infty \langle \lambda(s)\lambda(0)(\Delta J^2 - \langle \Delta J^2 \rangle) \rangle ds.$$  \hspace{1cm} (2)

where $\lambda(s)$ is the additional phase variable (defined in eq. (1) corresponding to a colour force of a system at time $s$ along a trajectory and $J$ is the colour 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 randomised, 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 [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 parallelisation 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, weighting for the number of timesteps executed on each processor. Further computational details of this experiment have been reported in [14]. Whilst the results of this experiment would appear meagre 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 Figures 2–9.

The TTCFs and their integrals are shown in figures 2–9. 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 [9], that the inverse nonlinear Burnett coefficients given by equation (2) should be intensive. As well as this, the 32 particle simulation shows strong evidence of a long time tail (Fig 2 and 3) when $Q_\lambda$ 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. 1, showing convergence within $t = 5$.

IV. CONCLUSION

This work presents strong numerical evidence in favour 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 [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.

V. ACKNOWLEDGEMENTS

The author wishes to thank the New South Wales Centre for Parallel Computing and the Fujitsu Parallel Computing Research Facilities for use of their facilities for this work. He would also like to thank Denis Evans for some helpful comments on the manuscript.
REFERENCES

[1] B. J. Alder and T. E. Wainwright, Phys. Rev. A 1, 18 (1970).
[2] M. H. Ernst et al., J. Stat. Phys. 18, 237 (1978).
[3] K. Kawasaki and J. D. Gunton, Physical Review A 8, 2048 (1972).
[4] J. J. Brey, R. Zwanzig, and J. R. Dorfman, Physica A 109, 425 (1981).
[5] M. H. Ernst and J. R. Dorfman, J. Stat. Phys. 12, 311 (1975).
[6] W. W. Wood, in Fundamental Problems in Statistical Mechanics III, edited by E. G. D. Cohen (North-Holland, Amsterdam, 1975).
[7] D. J. Evans and R. M. Lynden-Bell, Phys. Rev. A 38, 5249 (1988).
[8] R. K. Standish and D. J. Evans, Phys. Rev. A 41, 4501 (1990).
[9] R. K. Standish and D. J. Evans, Phys. Rev. E 48, 3478 (1993).
[10] B. L. Holian and W. W. Wood, in The Boltzmann Equation, Theory and Application, edited by E. G. D. Cohen and W. Thirring (Springer, NY, 1973), p. 451.
[11] D. J. Evans and G. P. Morriss, Phys. Rev. A 31, 3817 (1985).
[12] D. J. Evans, Mol. Phys. 80, 221 (1993).
[13] J. P. Hansen and I. R. McDonald, Theory of Simple Liquids, 2nd ed. (Academic, London, 1986).
[14] R. K. Standish, in Parallel Computing Workshop 97, edited by P. Mackerras (ANU, Canberra, 1997), pp. P2–W1, http://parallel.hpc.unsw.edu.au/rks.
FIG. 1. Integral of the TTCF for the Linear Transport Coefficient

FIG. 2. Transient Time Correlation Function for the 32 particle system with $Q_{\lambda} = 4.74$ at $1.32 \times 10^{11}$ timesteps
FIG. 3. Integral of TTCF for the 32 particle system with $Q_\lambda = 4.74$ at $1.32 \times 10^{11}$ timesteps

FIG. 4. Transient Time Correlation Function for the 32 particle system with $Q_\lambda = 1.4$ at $2.2 \times 10^{11}$ timesteps
FIG. 5. Integral of TTCF for the 32 particle system with $Q_\lambda = 1.4$ at $2.2 \times 10^{11}$ timesteps

FIG. 6. Transient Time Correlation Function for the 108 particle system at $1.1 \times 10^{11}$ timesteps
FIG. 7. Integral of TTCF for the 108 particle system at $1.1 \times 10^{11}$ timesteps

FIG. 8. Transient Time Correlation Function for the 256 particle system at $3 \times 10^{10}$ timesteps
FIG. 9. Integral of TTCF for the 256 particle system at $3 \times 10^{10}$ timesteps