Dense-fluid transport coefficients via the constrained-subtraction technique

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We have adopted the Lagrange-multiplier method, previously used to determine Lyapunov spectra, to the "subtraction technique" introduced by Ciccotti, Jacucci, and McDonald [J. Stat. Phys. **21**, 1 (1979)]. By adopting this approach we had hoped to minimize the influence of statistical fluctuations at long times on the linear response to external fields. We used Lagrange multipliers to constrain the phase-space separation $dr = (dq, dp)$ between two trajectories: an unperturbed equilibrium trajectory and a perturbed nonequilibrium trajectory. Although the Lagrange-multiplier constraint does eliminate much of the statistical noise, the correlations themselves are modified in an unacceptable way, artificially increasing the apparent diffusion coefficient while reducing the apparent heat conductivity.

I. INTRODUCTION

Transport coefficients for dense fluids have been evaluated by both indirect fluctuation methods as well as direct steady-state methods. In the indirect, Green-Kubo approach[1] the transport coefficients are related to the decay of equilibrium correlation functions. In the alternative direct approach,[2] nonequilibrium molecular dynamics, one measures the steady response to fields designed to generate mass, momentum, or energy currents. There are difficulties associated with both these approaches. On the one hand, statistical fluctuations make the Green-Kubo autocorrelation integrands hard to characterize at long times. The nonequilibrium steady-state simulations, on the other hand, need to be extrapolated to the zero-field limit, where the current vanishes, so that the results are again dominated by fluctuations.

To reduce the influence of the unwanted fluctuations, Ciccotti, Jacucci, and McDonald invented the "subtraction technique,"[3] in which nonequilibrium currents are first superimposed on the equilibrium fluctuating currents by using very small external fields. Next the unperturbed equilibrium current is subtracted. Then the resulting infinitesimal difference between perturbed and unperturbed currents is averaged over a few hundred pairs of trajectory "segments," with each segment containing a few hundred time steps. For times on the order of one or two collision times or less this procedure greatly enhances the signal-to-noise ratio. For somewhat longer times Lyapunov instability, the tendency for nearby trajectories to separate in phase space exponentially fast in time, predominates, and once again the quality of the information deteriorates. The present work developed in an effort to eliminate the effect of this Lyapunov instability on the differential currents generated by the subtraction technique.

It has recently been pointed out that the entire spectrum of Lyapunov exponents, which describe the chaotic comoving deformation of phase-space hypervolumes, can be determined by following the constrained motion of a set of orthogonal phase-space basis vectors.[4,5] In the present work we describe our attempts to adapt a similar approach to the transport-coefficient simulations. Although our results, described in the following section, show that this attempt has failed, it is nevertheless worthwhile to describe the work. In particular we hope it may stimulate others to reconsider the problem of overcoming statistical fluctuations, and perhaps to solve it, leading to more accurate evaluations of transport coefficients.

II. MODEL AND IMPLEMENTATION

We consider a Lennard-Jones potential,

$$\phi = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \, ,$$

joined smoothly at its inflection point at $(26/7)^{1/6}\sigma$ to a cubic-spline extension potential chosen to vanish at a cutoff distance, with zero slope. The four constraints of matching the two slopes and the two function values determine the range at which the potential is cut off, at approximately 1.74σ. We use a fourth-order Gear predictor-corrector algorithm, with a time step of 0.002 (using units such that the wall depth ϵ, mass m, and collision diameter σ are all set equal to 1). Although this time step is adequate for heat-flow calculations, in some of the mass-flow simulations a smaller time step, 0.001, was required.

We investigated both particle and energy currents for this potential by using δ-function impulsive forces applied to equilibrium trajectories. The new feature of the present work is the introduction of a phase-space constraint keeping the "distance" $dr = (dp^2 + dq^2)^{1/2}$ between two trajectories, an unperturbed equilibrium trajectory and the field-driven trajectory, constant after an initial interval of a few time steps. If we denote the vector separation in phase space between the two trajectories by the (many-dimensional) vector dr then the equation of motion becomes

$$d\dot{r} = d\dot{r}(r) - \lambda \cdot dr .$$

The time derivative of dr, $d\dot{r}(r)$ represents the time evolution of the trajectories' separation in the absence of constraints. The Lagrange multiplier λ, a scalar or tensor varying with time, has to be chosen to keep the scalar magnitude of dr fixed. In mass-flow simulations the constraint λ is a tensor chosen orthogonal to the stimulated current. In practice the equations determining λ and the resulting constrained time development of $dr, d\dot{r}$ have stable well-behaved solutions. Because dr contains both spatial and momentum components it might appear that the results would depend upon the mass, length, and time scales. We found that the results are insensitive to such variations.

Our preliminary calculations used 32 particles with periodic boundaries at a reduced density $N\sigma^3/V$ of 0.70 and a reduced temperature k_BT/ϵ of 2.68. We first used an external field which accelerates half the particles in the positive-x direction and half in the negative-x direction:

$$F_d = \pm F\tau\delta(0) .$$

Linear-response theory gives the diffusion coefficient in terms of integrated current density $\Sigma \pm p_x/(mV) = \langle J_x \rangle$ resulting from this impulsive driving force:

$$D = [(N-1)Vk_BT/F\tau N^2] \int \langle J_x \rangle dt .$$

In Fig. 1 we compare calculations in which the trajectories were kept constrained after times of 0.040 and 0.060 with the corresponding integrated current from an equilibrium Green-Kubo fluctuation calculation. The diffusion constants obtained from the constrained trajectories were 0.0080 and 0.0079, for constraints applied at these two times. The error in these results is of order 75%, compared to the accurate Green-Kubo value, 0.0048, with the constrained particle current greater than the driven one. The reason for the sign of the error is unclear. One might well expect that constraining the current to stay close to the equilibrium value, zero, would reduce, rather than enhance, the response. Our finding is the opposite.

Next we used a field sensitive to each particle's contributions to the energy and the pressure tensor[6,7] which generates a heat current consistent with the Green-Kubo heat conductivity, again at a reduced density of 0.7 but with a reduced temperature of 2.77, again using a field strength of order 10^{-5}, well within the linear regime.[8] We used both 108- and 256-particle systems and obtained very similar results. In Fig. 2 we show the 256-
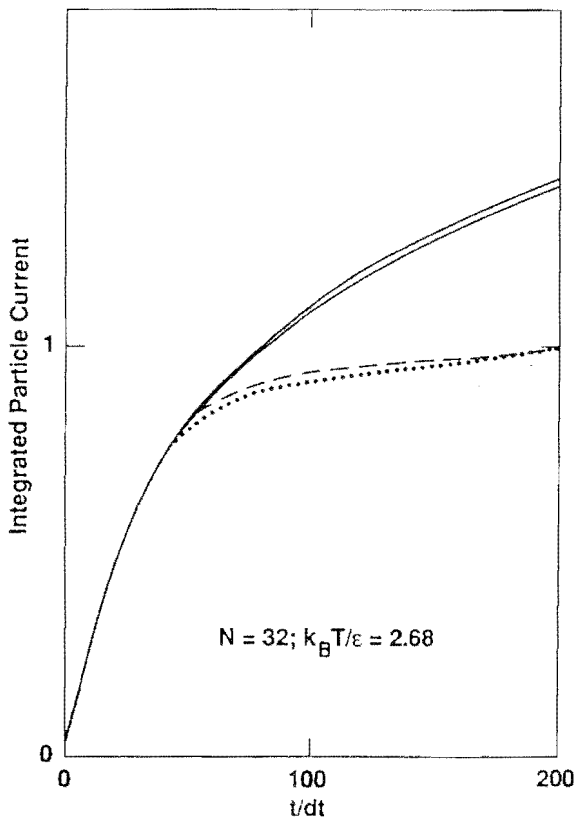

FIG. 1. Integrated 32-particle current, relative to the exact Green-Kubo value, for constraints applied at times of 0.040 and 0.060 (upper and lower solid lines). The unconstrained response (dotted line) for 600 separate segments and the prediction from a longer Green-Kubo calculation (dashed line) carried out for a quarter million-time steps are in good agreement with each other but lie far below the constrained response.
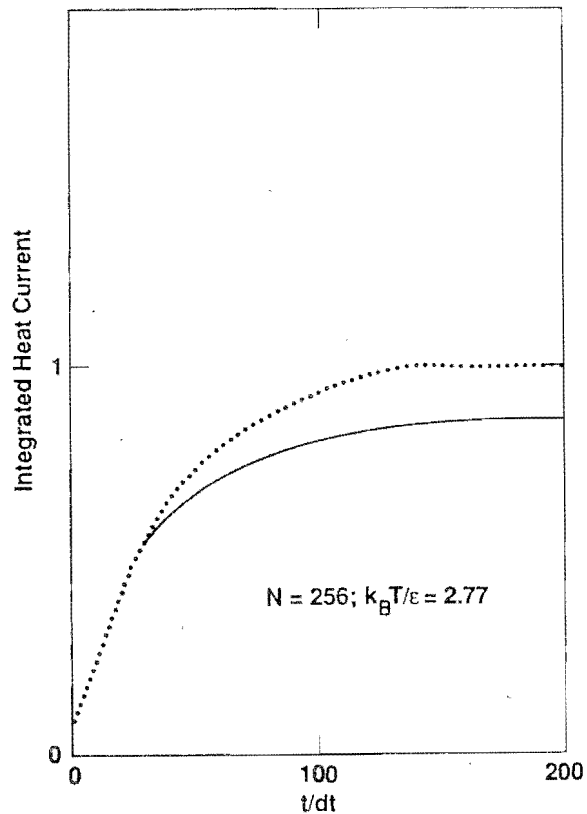

FIG. 2. Integrated 256-particle heat current, relative to the exact Green-Kubo value, for a constraint applied at time 0.040 (solid line) and for no constraint, averaged over 100 segments (dotted line), equivalent to a Green-Kubo evaluation of the heat conductivity.

particle data. The heat conductivity is reduced from the Green-Kubo value of 5.49 ± 0.53 to 4.75 ± 0.16. Thus the thermal conductivity, unlike the diffusion coefficient, is apparently reduced by the artificial constraint.

III. CONCLUSION

The phase-space constraints used here are too closely related to the induced signal (particle current or energy current) for the independence necessary to eliminate statistical noise. If an orthogonal constraint could be developed then conceivably this general idea could be made to work. But for the moment transport-coefficient calculations have to be pursued according to the existing equilibrium or nonequilibrium schemes.

IV. ACKNOWLEDGMENTS

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