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COMMENTS

Comment on "Modified nonequilibrium molecular dynamics for fluid flows with energy conservation" [J. Chem. Phys. 106, 5615 (1997)]

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(Received 5 May 1997; accepted 5 December 1997)

[S0021-9606(98)51910-1]

Tuckerman, Mundy, Balasubramanian, and Klein (TMBK) (Ref. 1) state that using a conserved "energy" H', enables them to derive a nonequilibrium steady state distribution function directly from the equilibrium microcanonical distribution function. There is, however, no justification for their application of Boltzmann's equilibrium equal-*a-priori*-probability assumption, away from equilibrium. The equal-*a-priori* assumption applies only to isolated equilibrium systems, and is conventionally used to justify equilibrium distribution functions.

In 1838 Liouville derived an equation of motion for the normalised nonequilibrium probability density, $f(\Gamma,t)$, of observing a phase $\Gamma\equiv(x_1,y_1,z_1,x_2,\ldots,p_{xN},p_{yN},p_{zN})$, for an N-particle system in a three-dimensional Cartesian space, at time t. In modern notation the equation he derived reads,[2]

$$\frac{\partial f(\Gamma,t)}{\partial t}=-\dot{\Gamma}\cdot\partial f(\Gamma,t)/\partial\Gamma-f(\Gamma,t)\partial\dot{\Gamma}\cdot/\partial\Gamma. \tag{1}$$

This equation is valid for non-Hamiltonian flows such as those employed in modern nonequilibrium molecular dynamics (NEMD) computer simulations.

Recently Evans and Searles[3] have shown that for ergostatted trajectories [i.e., constant internal energy, $H_0(\Gamma)\equiv\Sigma_i p_i^2/2m+\Phi(x_1,\ldots,z_N)$ where Φ is the potential energy], in which $\partial\dot{\Gamma}\cdot/\partial\Gamma=-3N\alpha+O(1)$, if one takes an *initial* equilibrium distribution function, for instance, the canonical distribution, $\exp[-\beta H_0(\Gamma)]/\int d\Gamma\exp[-\beta H_0(\Gamma)]$, and solves Eq. (1) then one can derive the following expression for $f(\Gamma,t)$:

$$f(\Gamma,t)=\exp\left\{-\int_0^{-t}3N\alpha[\Gamma(s)]ds\right\}f(\Gamma,0). \tag{2}$$

In Eq. (2) $\alpha(\Gamma)$ is a Lagrange multiplier chosen so that the internal energy is a constant of the motion. One can compute averages of phase functions, $B(\Gamma)$ in the usual ways,

$$\langle B(t)\rangle\equiv\int d\Gamma B(\Gamma(t))f(\Gamma,0)=\int d\Gamma B(\Gamma)f(\Gamma,t)$$
$$=\int d\Gamma B(\Gamma)\exp\left[3N\int_0^t ds\,\alpha(-s)\right]f(\Gamma,0). \tag{3}$$

From this approach it is clear that nonequilibrium phases with equal energies (in our example, *every accessible state*, since H_0 is a constant of the motion) are *not* equally probable. To dispel any doubt concerning this picture, we tested Eq. (3) using computer simulation.[3] Convincing agreement ($\pm0.3\%$) between the direct averaging and Eq. (3) was obtained for times up to ~84 times the reciprocal of the largest Lyapunov exponent of the system (or equivalently, ~4 times the time required for averages to achieve their steady state values; Fig. 2 of Ref. 3).

There is no justification for the TMBK assumption that nonequilibrium distribution functions can be derived using only *equilibrium* statistical mechanical arguments. Their "nonequilibrium" distributions are in fact, local equilibrium distribution functions. For shear flows, such local equilibrium distributions are clearly in error, because they imply an isotropic stress tensor without dissipation or shear stress.

There are other aspects of the TMBK paper[1] with which we are in profound disagreement but space limitations preclude a lengthy discussion. We list them here.

(a) TMBK (Ref. 1) argue that thermostatted nonequilibrium steady state distribution functions are smooth rather than fractal. They state that "it has recently been shown that for a nonequilibrium system... in the linear regime... the phase space is described by a smooth dis-

tribution function." However, the references they cite are not at all concerned with *thermostatted* nonequilibrium steady states, only with adiabatic nonequilibrium systems.

(b) TMBK (Ref. 1) criticize the numerical work establishing (i) the multifractal nature of thermostatted nonequilibrium distributions and (ii) the failure of chain thermostats to control temperature precisely. They claim these tests involved only low-dimensional systems. In fact such tests were carried out for systems with phase-space dimensions of several hundred.[7]

(c) It is clear from the literature[4] that the actual long time distributions are multifractal. A concrete test of the fractal nature of these distributions is provided by use of the Conjugate Pairing Rule, for the Lyapunov exponents of the steady state fractal, to compute the *numerical* values of transport coefficients for nonequilibrium steady states.[5]

Further, when applying the Conjugate Pairing Rule to calculate transport coefficients, the sum of the any conjugate pair of Lyapunov exponents is intensive,[5] for large enough N. This is consistent with the Kaplan–Yorke dimensional decrease in thermostatted nonequilibrium steady states, being *extensive*, again for large enough N.

Various properties concerning the nonequilibrium *distribution* of fluxes can be deduced equally well from conventional nonequilibrium response theory (3) or from the knowledge of the fractal properties of the nonequilibrium phase space distribution. The two approaches agree in both the linear[3] and nonlinear regimes.[6]

(d) TMBK (Ref. 1) state that Lees–Edwards boundary conditions are only accurate to $O(\Delta t^2)$ and are only consistent with the leapfrog integrator. In fact Lees–Edwards boundary conditions have nothing to do with particular numerical integration methods or with the timestep they employ.

(e) TMBK (Ref. 1) state that chain thermostats provide precise temperature control even far from equilibrium, provided a large number of degrees of freedom are employed. In fact, far from equilibrium, the temperature does not converge to the target value when chain thermostats are used.

(f) In Sec. IV,[1] TMBK consider a "thermostatted" fluid confined between two immobile boundaries subject to equations of motion[1] (16). In the absence of thermostatting, the system will obviously, at sufficiently long time, come to equilibrium with no shear. We note that in the absence of a thermostat, SLLOD is the same as Newton's equations [see TMBK Eqs.[1] (22)]. That they observe constant shear is due solely to their thermostat. In formulating their thermostat they *assume*, incorrectly, that the streaming velocity is a time independent linear function of y [see Ref. 1 Eq. (6)]. Their thermostat interprets all deviations from this assumed linear velocity profile as heat and then removes it. This *enforces* the stationary linear velocity profile they initially assumed. It is not the SLLOD algorithm which generates the long time shear within their geometry, it is the TMBK thermostat.

(g) The incorporation[1] of a history dependent Jacobian, $J(t;\mathbf{\Gamma})$, into the Liouville equation is ill-founded. The Jacobian is in fact already accounted for in nonequilibrium statistical mechanics. It can be obtained from the Lagrangian form

$$f(\mathbf{\Gamma}(t),t)=\exp\left[-\int_0^t 3N\alpha(\mathbf{\Gamma}(s))ds\right]f(\mathbf{\Gamma},\mathbf{0})$$

of the (Kawasaki) exponent[8] from which it is clear that

$$J(t;\mathbf{\Gamma}(0))\equiv|\partial\mathbf{\Gamma}(t)/\partial\mathbf{\Gamma}(0)|=\exp\left[-\int_0^t 3N\alpha(\mathbf{\Gamma}(s))ds\right]. \tag{4}$$

To convert our expressions into the notation of TMBK,[1] one should replace our $f(\mathbf{\Gamma}(t),t)$ by their $J(t;\mathbf{\Gamma}(0)f(\mathbf{\Gamma}(0),0)$. However, it should be noted that TMBK frequently forget the explicit time dependence of their Jacobian, J.

Finally, if the expression[1] used by Tuckerman, Mundy, Balasubramanian, and Klein for the steady state distribution function were correct, it would be possible to calculate steady state averages using Monte Carlo methods. This is in fact impossible.

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