127

Generalization of Nosé's isothermal molecular dynamics: Non-Hamiltonian dynamics for the canonical ensemble

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There are many potentially useful generalizations of Nosé's mechanics that are both deterministic and time reversible despite the lack of an underlying Hamiltonian. These generalizations are particularly useful in simulating systems far from equilibrium.

Jellinek and Berry[1,2] recently suggested generalizing Nosé's[3–5] Hamiltonian mechanics by introducing general coordinate-scaling and momentum-scaling functions to augment Nosé's time-scaling variable s. They suggested that this more general idea can improve our ability to simulate systems both at and away from equilibrium. I wish to comment here that many specific non-Hamiltonian, but still deterministic and time-reversible, generalizations are already available and can be readily implemented. A simple form of the non-Hamiltonian approach described below has very recently been extended to quantum systems.[6]

Consider first the canonical-ensemble equilibrium systems discussed by Jellinek and Berry[1,2] in their recent extension of Nosé's method. Nosé's method was naturally focused on the second moment of the equilibrium velocity distribution function. This is the natural choice to maintain consistency with the ideal-gas definition of absolute temperature. Thus the second-moment "Nosé-Hoover" equation of motion uses a friction coefficient ζ_1 which stabilizes the time-averaged value of $\langle p^2 \rangle = mkT$. The corresponding equation of motion, simplified to one dimension, is

$$\frac{dp}{dt} = F(q) - \zeta_1 p, \quad \frac{d\zeta_1}{dt} = \frac{p^2 - mkT}{mkT\tau^2} ,$$

and includes an arbitrary relaxation time τ. But it has been pointed out[7] that *other* moments can equally well be used:

$$\frac{dp}{dt} = F(q) - \zeta_3 p^3, \quad \frac{d\zeta_3}{dt} = \frac{p^4 - 3p^2 mkT}{(mkT)^2\tau^2} ,$$

$$\frac{dp}{dt} = F(q) - \zeta_5 p^5, \quad \frac{d\zeta_5}{dt} = \frac{p^6 - 5p^4 mkT}{(mkT)^3\tau^2} .$$

By following the arguments outlined in Refs. 5 and 7, it is evident that *general* linear combinations of thermostatting forces, $-\sum \zeta_n p^n$, can be made consistent with the equilibrium canonical distribution augmented by a Gaussian distribution in the set of friction coefficients $\{\zeta_n\}$. It is not yet known if these non-Hamiltonian equations of motion can be described by applying the general Hamiltonian treatment introduced by Jellinek and Berry.

These equilibrium ideas can be extended to classical nonequilibrium many-body systems. In the simplest case—homogeneous, steady, isothermal, field-driven diffusion[8,9]—Nosé's time-scaling variable s is applied to each particle's momentum and the resulting phase-space motion has an *exact* Hamiltonian analog. That is, the coordinates q and the unscaled momenta p follow the *same qp* trajectories in the equilibrium-Hamiltonian and driven-non-Hamiltonian "scaled" cases. The Hamiltonian analog trajectory can be followed computationally for only a short time, and is *non*steady, because Nosé's time-scale factor s increases exponentially with time.

But "realistic" boundary-driven inhomogeneous problems such as heat flow or shear flow between reservoirs are more complex. Such flows necessarily involve *different* "Hamiltonian" time scales for different degrees of freedom. In the simplest case, bulk Newtonian fluid would move in "ordinary" unscaled time, while the driving reservoir degrees of freedom would have to evolve at different rates, scaled with local values of Nosé's s. Such systems therefore lack a Hamiltonian analog.

But the equations of motion describing these inhomogeneous nonequilibrium systems are nevertheless deterministic and time reversible. The two latter features make it possible to show in detail that these steady nonequilibrium systems obey the second law of thermodynamics. They avoid the reversibility paradox of Loschmidt by occupying a phase-space strange attractor with Kaplan-Yorke dimensionality less than the equilibrium phase-space dimension considered by Jellinek and Berry.[10] The non-Hamiltonian generalizations of Nosé's mechanics have also the desirable feature that they are directly related to the Sonine velocity polynomials used in kinetic-theory expansions of nonequilibrium distribution functions.

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