

Time-reversible equilibrium and nonequilibrium isothermal-isobaric simulations with centered-difference Stoermer algorithms

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(Received 17 January 1990)

We describe simple, stable, and economical numerical methods for implementing temperature and pressure controls in equilibrium and nonequilibrium Nosé-Hoover dynamics. These methods substantially increase the efficiency of large-scale simulations.

We are presently carrying out a wide range of atomistic computer simulations to elucidate the size dependence, rate dependence, and temperature dependence of irreversible material behavior in fracture and flow. The simulations considered to date have covered a range of sizes up to 10^6 atoms in two dimensions. Using the Lennard-Jones spline potential,¹ million-particle simulations take just over 30 s per time step on the 64-transputer multiprocessor SPRINT (Ref. 2) at Livermore. This machine provides the computational speed of a CRAY at 1/1000 of the cost. To minimize the computer-storage requirements of these simulations we have developed and used modified Stoermer versions of Nosé-Hoover isothermal and isobaric equilibrium and nonequilibrium molecular dynamics.³ The time reversibility of the resulting dynamics is limited only by computer rounding. The methods are highly stable.

In all of these simulations the kinetic temperature T is maintained by integral feedback, using Nosé's time-reversible friction coefficient ζ . It is usual to solve these equations with Runge-Kutta, Gear, or predictor-corrector methods, but these require from 3 to 10 times the storage of the simpler Stoermer-based algorithms. A straightforward approach to implementing Nosé's isothermal equations of motion,

$$d^2\mathbf{r}/dt^2 = [F(\mathbf{r})/m] - \zeta(t)(d\mathbf{r}/dt),$$

$$d\zeta/dt = \{[K(t) - K_{av}]/K_{av}\}/\tau^2,$$

involves solving the centered finite difference form for the

new coordinates r_+ in terms of the present and previous coordinates, r_0 and r_- , and using the current friction coefficient ζ_0 :

$$(r_+ - 2r_0 + r_-)/(dt)^2 = F_0/m - \zeta_0(r_+ - r_-)/(2dt).$$

The new coordinates can then be used to determine a new value for the friction coefficient ζ_+ using a centered kinetic energy $K_{1/2}$ calculated from the coordinates r_+ and r_0 ,

$$\zeta_+ - \zeta_0 = [(K_{1/2} - K_{av})/K_{av}](dt)/\tau^2.$$

$K_{av} = DNkT/2$ is the equipartition, long-time-averaged value of the kinetic energy in D dimensions at the specified temperature T and τ is an arbitrary thermostat relaxation time.

These centered equations are very simple to program and are numerically very stable. Useful results for the Lennard-Jones potential can be obtained with time steps up to $0.02(m\sigma^2/\epsilon)^{1/2}$. It should be noted that the maximum time-step size satisfying linear stability analysis varies slowly with system size, typically as $(\ln N)^{-1/2}$.

We have verified the stability and accuracy of general isobaric-isothermal versions of Nosé's mechanics.³ These equations involve both a friction coefficient ζ and a strain rate $\dot{\epsilon}$, in addition to the (reduced) particle coordinates $\{x\} = \{rV^{-1/D}\}$ which vary from 0 to 1. D is the dimensionality of the system, usually 2 or 3. A straightforward centered-difference scheme can be applied to these isobaric-isothermal cases, too. The corresponding difference equations are expressed in terms of the reduced coordi-

ates,

$$(x_+ - 2x_0 + x_-)/dt^2 = (F_0/m)V_0^{-1/D} \\ - (\zeta_0 + 2\dot{\epsilon}_0)(x_+ - x_-)/2dt,$$

$$\dot{\epsilon}_0 = (V_+ - V_-)/2DV_0dt,$$

$$(\dot{\epsilon}_+ - \dot{\epsilon}_-)/2dt = V_0\Delta P_0/kT\tau^2,$$

$$(\zeta_+ - \zeta_-)/2dt = \Delta K_0(2/Q).$$

These four equations can be solved in a series of explicit steps: (1) compute x_+ from the first equation; (2) compute V_+ from the second equation; (3) compute $\dot{\epsilon}_+$ from the third equation; (4) compute ζ_+ from the fourth equation.

Just as in the simpler isothermal case these constant-pressure constant-temperature equations are exactly time reversible, stable, and accurate. We recommend their use and expect to report the detailed results of our large-scale simulations in due course.

We thank Professor Shuichi Nosé, Professor Toshio Kawai, Professor Harald Posch, and Dr. Sigeo Ihara for stimulating conversations. Parts of this work, performed at the Lawrence Livermore National Laboratory and the Los Alamos National Laboratory, were supported by the U.S. Department of Energy under University of California Contracts No. W-7405-Eng-36 and No. W-7405-Eng-48. The remainder of this work was performed at Keio University, in Yokohama, and was supported by the Japan Society for the Promotion of Science.

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