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europhysics
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abstracts

EUROPHYSICS LIQUID STATE CONFERENCE
ON
LIQUIDS OF SMALL MOLECULES

SANTA TRADA (REGGIO CALABRIA) - ITALY

21-25 SEPT. 1987 28 29 30 1 2
14-18
7-11

Published by: European Physical Society

Series Editor: Prof. S. Methfessel, Bochum

Managing Editor: G. Thomas, Geneva
Volume Editor: M. Nardone, Roma

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Chaotic dynamics in dense fluids

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We present calculations of the full spectra of Lyapunov exponents for 8- and 32-particle systems with periodic boundary conditions and interacting with the repulsive part of a Lennard-Jones potential both in equilibrium and nonequilibrium steady states. Lyapunov characteristic exponents λ_n describe the mean exponential rates of divergence and convergence of neighbouring trajectories in phase-space. They are useful in characterizing the stochastic properties of a dynamical system. A new algorithm for their calculation is presented which incorporates ideas from control theory and constraint nonequilibrium molecular dynamics [1,2].

For the simulations isokinetic equations of motion based on Gauss's principle of least constraint are used, which are a limiting case of the even more general isothermal mechanics invented by S. Nosē. Nonequilibrium steady states are generated by the application of an external field F_e through which an equal number of particles are accelerated in opposite directions. In equilibrium with no external field applied ($F_e = 0$), the Lyapunov spectra are symmetrical around zero and the sum over all exponents vanishes. This is shown in the figure for an equilibrium 32-body fluid (reduced density = 0.5, reduced temperature $\doteq$ 1.0). The smooth line is the fit of a power law, $\lambda = \alpha n^\beta$, to the data, where n is the number of positive exponents less or equal to a given value of λ. All quantities are given in reduced units with the Lennard-Jones parameters σ, ϵ and the particle mass m acting as units of length, energy and mass, respectively. We find $\alpha = 0.63$ and $\beta = 0.38$. Such a power law may be derived from the simple Debye model for vibrational frequencies in solids with $\beta_{Debye} = 1/3$. The maximum Lyapunov exponent is also close in value to the Debye frequency.

For nonequilibrium steady states ($F_e \neq 0$) the Lyapunov spectra are not symmetrical and the sum over all Lyapunov exponents is negative. This means that the distribution function eventually diverges to infinity

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indicating a collapse of the phase-space probability onto a subspace of zero volume. This subspace is a fractal attractor as found previously in simpler systems [3,4]. In these steady-state systems the energy supplied by the external field is continuously dissipated and removed by the thermostat. However, the Gauss and Nosē equations of motion are invariant with respect to time reversal. The only trajectories which could violate the Second Law would have to start on the repeller states obtained from the fractal attractor by a time reversal transformation. Since the repeller is also a fractal with zero volume in phase-space, the probability of such trajectories to occur is zero. Thus Nosē mechanics resolves the old reversibility paradox of Loschmidt for nonequilibrium steady states.

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