Effect of Molecular Fluctuations on the Description of Chaos by Macrovariable Equations

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Intrinsic molecular fluctuations are associated with macrovariables whose time evolution is described by macrovariable equations. When the macrovariable equations describe chaotic trajectories, the covariance matrix for the molecular fluctuations diverges rapidly. This implies that the macrovariable equations are not stable and cannot be justified from an underlying molecular description.

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There is a long tradition behind the description of macroscopic dissipative processes by phenomenological equations, e.g., hydrodynamics, electrical circuits, and mass-action chemical reactions. It is now widely appreciated[1-9] that a complete macroscopic description of these processes must include the deterministic macrovariables as well as their molecular fluctuations, both of which reflect underlying microscopic dynamics.[1,2,8,9] Indeed, these fluctuations provide the basis for our understanding of light scattering,[10,11] electrical noise, and other noise measurements for macroscopic systems.[12]

By considering the thermodynamic limit of Hamiltonian, kinetic theory,[13] and master equation theories,[14-22] numerous investigators have concluded that fluctuations in macroscopic variables—such as the mass, momentum, and internal energy densities used in hydrodynamics—satisfy Langevin-type equations obtained by linearization around the usual phenomenological macrovariable equations. While these equations successfully describe a variety of physical and chemical phenomena for both stationary and nonstationary states,[8,12] recent numerical work suggests that this approach breaks down on chaotic attractors.[23] Here we investigate this phenomenon further by applying hydrodynamic fluctuation theory to the Lorenz model. We show by numerical calculations that the trace norm of the covariance matrix diverges exponentially at twice the rate of the largest Lyapunov exponent. This is a general property of linearized Langevin theories on chaotic attractors, a result that is discussed here but whose proof is reserved for elsewhere.[24]

We focus on the Lorenz model[25] because it has its origins in the hydrodynamic equations (using constitutive relations and thermodynamic identities the internal energy density is replaced by the temperature density,[7,26] for which there is a generally agreed upon hydrodynamic fluctuation theory).[7,9-11] The Lorenz model exhibits chaos in an appropriate parameter range and can be interpreted as a macroscopic, three-mode representation of the Rayleigh-Bénard problem. The well-known, approximate, Galerkin truncation[25] leads to the following coupled equations for the lowest-order amplitudes (macrovariables) of the temperature deviation (Y and Z) and vorticity (X):

$$\frac{d}{dt}X=-\sigma(X-Y)\,,\quad \frac{d}{dt}Y=-XZ+rX-Y\,,\quad \frac{d}{dt}Z=XY-bZ\,. \tag{1}$$

According to fluctuating hydrodynamics,[7,8,12,26] Eq. (1) represents the conditionally averaged behavior of the amplitudes. Molecular fluctuations in the amplitudes can be obtained in a similar fashion by analyzing fluctuations in the mass, momentum, and temperature densities for the Rayleigh-Bénard problem. Since the fluctuations satisfy linearized equations obtained from the hydrodynamic equations,[7,26] a Galerkin truncation paralleling that used to obtain the Lorenz equations also yields the associated fluctuation equations. Denoting the fluc-

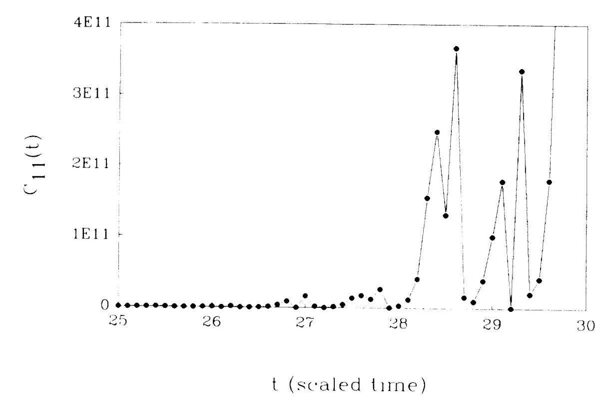

FIG. 1. The variance for δX, C_{11}, grows large and varies wildly.

tuations in X, Y, and Z by δX, δY, and δZ, we obtain[24]

$$\begin{aligned}\frac{d}{dt}\delta X &= -\sigma(\delta X-\delta Y)+f_X ,\\ \frac{d}{dt}\delta Y &= -X\delta Z - Z\delta X + r\delta X - \delta Y + f_Y ,\\ \frac{d}{dt}\delta Z &= X\delta Y + Y\delta X - b\delta Z + f_Z ,\end{aligned} \tag{2}$$

in which f_X, f_Y, and f_Z are the derived Gaussian fluctuating forces.[7,26]

Equation (2) is coupled to Eq. (1) via the Jacobian matrix of coefficients, $\mathbf{J}$, which depends explicitly on the time-dependent solution to Eq. (1):

$$\mathbf{J}=\begin{bmatrix}\frac{\partial dX/dt}{\partial X} & \frac{\partial dX/dt}{\partial Y} & \frac{\partial dX/dt}{\partial Z}\\ \frac{\partial dY/dt}{\partial X} & \frac{\partial dY/dt}{\partial Y} & \frac{\partial dY/dt}{\partial Z}\\ \frac{\partial dZ/dt}{\partial X} & \frac{\partial dZ/dt}{\partial Y} & \frac{\partial dZ/dt}{\partial Z}\end{bmatrix} = \begin{bmatrix}-\sigma & \sigma & 0\\ r-Z & -1 & -X\\ Y & X & -b\end{bmatrix} . \tag{3}$$

It is well known[8,12] that the stochastic differential equations, Eq. (2), produce a nonstationary, Gaussian conditional probability distribution with vanishing mean and covariance matrix, $\mathbf{C}$, defined by

$$\mathbf{C}=\begin{bmatrix}\langle\delta X\delta X\rangle & \langle\delta X\delta Y\rangle & \langle\delta X\delta Z\rangle\\ \langle\delta Y\delta X\rangle & \langle\delta Y\delta Y\rangle & \langle\delta Y\delta Z\rangle\\ \langle\delta Z\delta X\rangle & \langle\delta Z\delta Y\rangle & \langle\delta Z\delta Z\rangle\end{bmatrix} , \tag{4}$$

which solves the equation

$$\frac{d\mathbf{C}}{dt}=\mathbf{J}\mathbf{C}+\mathbf{C}\mathbf{J}^{\dagger}+\mathbf{\Gamma} \tag{5}$$

and in which $\mathbf{\Gamma}$ is the matrix of correlation coefficients for the fluctuating forces in Eq. (2). This matrix is completely determined by the fluctuation-dissipation relation for hydrodynamics and involves no free parameters.[26] Its explicit form will be given elsewhere,[24] but we note here that each coefficient is proportional to Boltzmann's constant. The solution of Eq. (5) is easily generated numerically[8,23] using the conditional average solution obtained from Eq. (1).

Note that there are two types of stochasticity here: deterministic stochasticity from the chaotic macrovariable dynamics [Eq. (1)], and molecular fluctuations coming from thermal motions [Eq. (2)]. This is typical of the thermodynamic limit[3-22] in that the thermal fluctuations "ride on the back" of the deterministic motion.

The solution for the covariance matrix is easily obtained using standard differential equation solvers with initial conditions on the chaotic attractor and a covariance matrix that initially vanishes. Figure 1 shows the results for the parameter values $\sigma=10$, $b=\frac{8}{3}$, and $r=28$, for which the Lorenz model is chaotic. The one-one element of the covariance matrix (δX-mode variance) is seen both to grow and to fluctuate wildly as it rides along the attractor. Comparable results are found for other matrix elements. Keizer and Tilden[23] previously conjectured that the covariance matrix grows exponentially on a chaotic attractor at twice the rate of the largest positive Lyapunov exponent. In fact, we have found a way to make this conjecture precise[24] using the trace norm, as illustrated by the plot in Fig. 2 of the logarithm of the square root of the trace of the covariance matrix squared. This smooths out the plot enormously, which after a few time units essentially increases linearly with the time. The slope of this linear plot is 1.84, which is precisely twice the largest positive Lyapunov exponent for the attractor as determined by standard methods.[27]

The exponential growth of fluctuations on the chaotic attractor has striking consequences. First, when the square root of a covariance becomes comparable to the size of the macroscopic variables, the deterministic equations lose their meaning. According to Fig. 2, this becomes the case at a scaled time of approximately 20. Using values of the density, viscosity, and aspect ratio typical for water and the Rayleigh-Bénard system, we estimate the actual time required for this to occur in the Lozenz model is about 40 min. This suggests that in hydrodynamic experiments on chaotic systems, the effect of fluctuations may be amplified to macroscopic size on an experimentally accessible time scale. Second, this result suggests that on this time scale the macroscopic, deterministic description for the hydrodynamic variables may break down. A detailed analytic account of this breakdown will appear elsewhere.[24]

The exponential divergence of the covariance matrix for dissipative macrovariable fluctuations on a chaotic attractor is a general property of the usual fluctuation theories in the thermodynamic limit.[8,12,24] In this limit, the macrovariables satisfy the usual kinetic equations [cf. Eq. (1)], and the covariance matrix for the fluctuations solves an equation with exactly the same form as

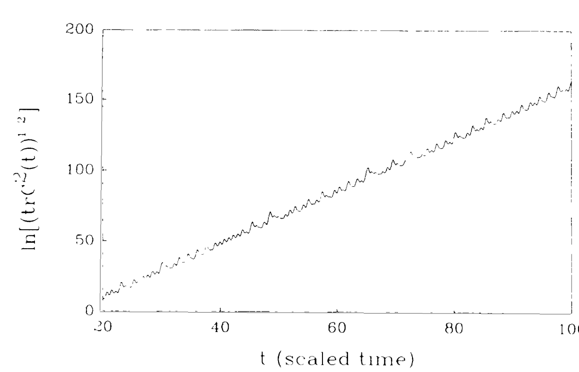

FIG. 2. The Lyapunov exponent is one-half of the slope, i.e., 0.92.

Eq. (5) where $\mathbf{J}$ is the Jacobian matrix for the macrovariable motion and Γ is the strength of the correlation coefficients for the Gaussian forces. For the coupled system of macrovariables and covariance matrix, it is not difficult to show, either numerically or analytically, that asymptotically in time, on a chaotic attractor, the covariance matrix grows at twice the rate of the largest Lyapunov exponent.[23,24] Specifically, we find that it is possible to define a Lyapunov exponent for the covariance matrix equation [Eq. (5)], denoted by λ_C, and we have proved the identity

$$\lambda_C = 2\lambda , \tag{6}$$

where λ is the Lyapunov exponent for the deterministic macrovariable equation. The proof of this identity follows from the fact that the Jacobi matrix not only determines the time evolution of the covariance matrix [Eq. (5)], but is also responsible for determining the Lyapunov exponent λ for the macrovariable equations.[27] Thus the observed behavior of the fluctuating Lorenz model in the thermodynamic limit is generic.

As a consequence, we expect that, (1) on the time scale of the inverse of the largest (positive) Lyapunov exponent, the average behavior will not be correctly given by the deterministic equations, and (2) on this time scale, molecular fluctuations are sufficiently amplified that a molecular-level description must be used instead of a purely macrovariable description.

It should be emphasized that these results refer only to macroscopic systems for which the dynamical processes are dissipative. For example, they do not apply to conservative Hamiltonian systems in which chaos is also well established. However, they seem relevant for chaotic dynamics in chemistry, as well as in various kinds of hydrodynamic systems. Finally, numerical calculations suggesting that turbulence involves a chaotic attractor make us suspect that a complete description of experimental turbulence will require more than just the Navier-Stokes equations; a more molecular-level description will be necessary.

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