Chaos, molecular fluctuations, and the correspondence limit

Ronald F. Fox
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430
(Received 31 October 1989)

Chaos is characterized by sensitive dependence on initial conditions. Trajectories determined by coupled, ordinary differential equations show sensitive dependence when their associated Liapunov exponent is positive. The Liapunov exponent is positive if the Jacobi matrix associated with the coupled differential equations has an eigenvalue with a positive real part, on the average, as the Jacobi matrix evolves along the trajectory. For macrovariable equations, there are also fluctuation equations which follow the macrovariable trajectories. The covariance matrix for these fluctuations evolves according to an equation in which the Jacobi matrix for the deterministic motion plays the dominant role. For a chaotic trajectory, the covariance matrix grows exponentially. This means that for macrovariable equations that imply chaos, the construction of the macrovariable equations out of an underlying master equation is no longer valid. The macrovariable equations cease to be physical, and the physical description must be done entirely at the master equation level of description where the fluctuations, which are very large scale, can be properly treated. In parallel with this analysis, the correspondence limit connecting the time evolution of the Wigner distribution with Liouville's equation breaks down when the classical motion is strongly chaotic. This implies that strongly chaotic classical dynamics must be treated quantum mechanically in order to properly treat the quantum fluctuations which have grown macroscopically large. Experimental confirmation of these ideas is discussed.

I. WHAT IS CHAOS?

Consider a system of coupled, first-order differential equations of the form

$$\frac{d}{dt}x_i(t)=F_i(\mathbf{x}(t)) , \tag{1}$$

where $i=1,2,\ldots,N$ and $\mathbf{x}(t)$ denotes the N-dimensional vector with components x_i. The functions F_i are generally nonlinear. Because these equations are first order in the time derivative, initial conditions give rise to unique trajectories. Chaos is very sensitive dependence of the trajectory $\mathbf{x}(t)$ on the initial conditions.

This sensitive dependence can be made quantitative by introducing the concept of a Liapunov exponent.[1] First, consider the instantaneous, local linearization around the trajectory $\mathbf{x}(t)$. Let $\Delta\mathbf{x}$ denote a small deviation from $\mathbf{x}(t)$ at time t. For a short time, $\Delta\mathbf{x}$ evolves according to

$$\frac{d}{dt}\Delta x_i=J_{ik}\Delta x_k , \tag{2}$$

in which summation over k is implicit and J_{ik} is the Jacobi matrix defined by

$$J_{ik}=\frac{\partial F_i}{\partial x_k} . \tag{3}$$

The nonlinearity of the F_i's implies that J_{ik} is an explicit function of $\mathbf{x}(t)$. As the trajectory evolves in time, the matrix elements J_{ik} also evolve. At each instant of time, one may compute the eigenvalues of J_{ik}. If at least one eigenvalue has a positive real part, there is an instantaneous, local tendency for the magnitude of $\Delta\mathbf{x}$ to grow, along a direction corresponding to the associated eigenvector. As the trajectory evolves, and J_{ik} also evolves, such a tendency is averaged over the course of the trajectory and this leads to the definition of the Liapunov exponent.

Let

$$d(\mathbf{x}_0,t)=\|\Delta\mathbf{x}(\mathbf{x}_0,t)\| \tag{4}$$

be the length of the deviation vector at time t that started at $t=0$ from $\mathbf{x}=\mathbf{x}_0$. We have used the notation $\|\ \|$ for the Euclidean metric in an N-dimensional space. The Liapunov exponent λ is defined by[1]

$$\lambda=\lim_{\substack{t\to\infty \\ d(\mathbf{x}_0,0)\to 0}}\frac{1}{t}\ln\left[\frac{d(\mathbf{x}_0,t)}{d(\mathbf{x}_0,0)}\right] . \tag{5}$$

If $\lambda>0$, then initially close trajectories exponentiate apart with an initial rate λ. This is what is meant by sensitive dependence on initial conditions. If (1) describes a dissipative dynamics and parameters are chosen so that trajectories approach a globally stable attracting fixed point, then $\lambda<0$. If a limit cycle is the attractor, then $\lambda=0$. But if the attractor is that for a chaotic trajectory (dissipative or Hamiltonian dynamics), then $\lambda>0$.

There is another representation of the dynamics in (1) which will prove useful below. We may describe the dynamics in (1) by a conserved probability flow for the probability distribution $P(\mathbf{x},t)$:

$$\frac{\partial}{\partial t}P(\mathbf{x},t)=-\frac{\partial}{\partial x_j}[F_j(\mathbf{x})P(\mathbf{x},t)] , \tag{6}$$

with the initial condition $P(\mathbf{x},0)=\delta(\mathbf{x}-\mathbf{x}_0)$. Equation (6)

is simply the continuity equation for a conserved probability flow with probability flux $\mathbf{F}P$. Since it is first order on both the left- and right-hand sides, it is straightforward to prove that it has the solution

$$P(\mathbf{x},t)=\delta(\mathbf{x}-\mathbf{x}(t)) , \tag{7}$$

where $\mathbf{x}(t)$ is the solution to Eq. (1). Clearly, if we multiply (6) by x_i and integrate over $d^N x$ we get

$$\frac{d}{dt}\langle x_i \rangle = \langle F_i(\mathbf{x}) \rangle , \tag{8}$$

where $\langle\ \rangle$ denotes averaging with respect to $P(\mathbf{x},t)$. Since (7) holds, Eqs. (1) and (8) are identical. Because this probability distribution remains a Dirac δ function for all times, it describes a deterministic motion with no fluctuation whatsoever around the deterministic trajectories implied by (1).

We remark in passing that, although (6) is a linear equation in P, it nevertheless describes chaos. Whenever the $\mathbf{x}(t)$ trajectory is chaotic, the P distribution simply follows the $\mathbf{x}(t)$ trajectory, and also exhibits chaos. One may think of (6) as an example of Liouville's equation, the name we use for it below.

The key points developed here are that the magnitude of the Liapunov exponent is determined by the time-evolving Jacobi matrix, and that Liouville's equation provides a description of the dynamics equivalent to (1) when its solution is the Dirac δ function solution that follows the trajectory. In the following sections of this paper, we will return to these key points for the discussions of both molecular fluctuations and the correspondence limit.

II. MOLECULAR FLUCTUATIONS

Macrovariable equations are phenomenological descriptions of physical or chemical phenomena at the macroscopic level rather than many-particle descriptions at the fundamental microscopic level. We briefly discuss two examples below: hydrodynamics and chemical reactions.

The hydrodynamic equations are[2]

$$\frac{\partial}{\partial t}\rho = -\nabla\cdot(\rho\mathbf{u}) , \tag{9}$$

$$\rho\left(\frac{\partial}{\partial t}u_\alpha + \mathbf{u}\cdot\nabla u_\alpha\right) = -\frac{\partial}{\partial x_\beta}P_{\alpha\beta} , \tag{10}$$

$$\rho\left(\frac{\partial}{\partial t}\varepsilon + \mathbf{u}\cdot\nabla\varepsilon\right) = -\nabla\cdot\mathbf{q} - P_{\alpha\beta}D_{\alpha\beta} , \tag{11}$$

in which ρ is the mass density, $\mathbf{u}$ is the velocity field, ε is the energy field per unit mass, $P_{\alpha\beta}$ is the stress tensor, $\mathbf{q}$ is the heat flux, and $D_{\alpha\beta}$ is the strain tensor. In this form, these equations represent conservation of mass, momentum, and energy, respectively. They do not constitute a closed description,[3] however, because the quantities on the right-hand side, such as $P_{\alpha\beta}$ and $\mathbf{q}$, are not expressed solely in terms of the quantities of the left-hand side. This can be remedied by introducing the constitutive relations and equations of state which then produce a well-posed mathematical description. Usually, one ends up with a closed description in the quantities ρ, $\mathbf{u}$, and T where T is the temperature field. Because these quantities represent macroscopic amounts of matter, they have associated with them molecular fluctuations.[4,5] For example, in the description of the hydrodynamics of water, ρ, $\mathbf{u}$, and T may refer to the quantities found for a cubic micrometer of water (this is a "macroscopic" amount) which contains $\sim 10^{11}$ water molecules. From the macroscopic viewpoint, the cubic micrometer is thought of as a point, but there will be molecular fluctuations associated with ρ, $\mathbf{u}$, and T. The theory for these fluctuations is well worked out and is used to compute light scattering profiles that have been repeatedly confirmed with measurements.[6]

A bimolecular reaction

$$A + B \underset{k_b}{\overset{k_f}{\rightleftarrows}} C + D \tag{12}$$

is described by the mass action equation[7]

$$\frac{d}{dt}\xi = k_f C_A C_B - k_b C_C C_D , \tag{13}$$

in which C_A, etc. are the concentrations of the various chemical species and ξ is the reaction progress variable. C_A is the concentration of species A in the total volume of the reaction and no spatial variations are contemplated. This situation is realized from a macroscopic viewpoint in a "continuously stirred tank reactor." Nevertheless, chemicals are molecules and each concentration has associated with it a molecular fluctuation. Once again, the theory for such fluctuations is well established.[7-9]

A rather general theoretical approach has been developed to deepen our understanding of how fundamental microscopic dynamics gives rise to macroscopic, deterministic equations and their associated molecular fluctuation equations. This is the master equation approach.[8,10] In essence, it is a mesoscopic description of dynamics, intermediate between the truly microscopic, many-particle dynamics and the macroscopic phenomenology. For mass action chemical reactions, the McQuarrie master equation[8] is very well established.[9] For dilute gas hydrodynamics, Boltzmann's equation serves the role of the master equation,[3,5] and for moderately dense gases the Boltzmann-Enskog equation does likewise.[11,12] For liquids, however, no master equation or equivalent is widely accepted, so that one of the upshots of the proposals to be enunciated below will be establishing such a master equation construct for hydrodynamics in order to use it to test other of our proposals. Modern kinetic theory may have already taken us a long way towards this particular goal.

All master equations may be put into the form[10]

$$\frac{\partial}{\partial t}P(\mathbf{c},t) = \int d^N c'[W(\mathbf{c},\mathbf{c}')P(\mathbf{c}',t) - W(\mathbf{c}',\mathbf{c})P(\mathbf{c},t)] , \tag{14}$$

in which $\mathbf{c}$ and $\mathbf{c}'$ denote the macrovariables, $P(\mathbf{c},t)$ is the probability distribution for the macrovariables at time t, and $W(\mathbf{c},\mathbf{c}')$ is the transition distribution for changes in

the macrovariables. $W(\mathbf{c},\mathbf{c}')$ determines how much $\mathbf{c}'$ changes in an infinitesimal time interval, Δt. Normally, this change is by a molecular amount, but at a macroscopic rate. This means the following. Let Ω characterize the macroscopic size of the system (e.g., Ω could be the total volume). Normally, W causes a change in $\mathbf{c}'$ components of size $1/\Omega$ at a rate $\sim\Omega$. We may make this quantitative by looking at the moments of W:

$$K_i^{(1)}(\mathbf{c})=\int d^N c'(c_i'-c_i)W(\mathbf{c}',\mathbf{c}) , \tag{15}$$

$$K_{ij}^{(2)}(\mathbf{c})=\int d^N c'(c_i'-c_i)(c_j'-c_j)W(\mathbf{c}'\mathbf{c}) , \tag{16}$$

$$\vdots$$

$$K_{i_1 i_2 \cdots i_p}^{(p)}(\mathbf{c})=\int d^N c' \prod_{j=1}^{p}(c_{i_j}'-c_{i_j})W(\mathbf{c}',\mathbf{c}) . \tag{17}$$

The preceding remarks imply that for large Ω, $K^{(p)}\sim\Omega^{-(p-1)}$. In addition, it may be shown that the master equation (14) is equivalent to the Kramers-Moyal[13–15] partial differential equation

$$\frac{\partial}{\partial t}P=-\frac{\partial}{\partial c_i}(K_i^{(1)}P)+\frac{1}{2}\frac{\partial^2}{\partial c_i \partial c_j}(K_{ij}^{(2)}P)+\cdots + \frac{(-1)^p}{p!}\prod_{j=1}^{p}\frac{\partial}{\partial c_{i_j}}(K_{i_1 i_2 \cdots i_p}^{(p)}P)+\cdots . \tag{18}$$

We are now in a position to take the "macroscopic limit," i.e., $\Omega\to\infty$. The result is the first-order Liouville equation:[15–17]

$$\frac{\partial}{\partial t}P_\infty=-\frac{\partial}{\partial c_i}(K_i^{(1)\infty}P_\infty) . \tag{19}$$

This equation has the Dirac δ solution

$$P_\infty(\mathbf{c},t)=\delta(\mathbf{c}-\mathbf{c}(t)) , \tag{20}$$

where $\mathbf{c}(t)$ solves the equation

$$\frac{d}{dt}c_i(t)=K_i^{(1)\infty}(\mathbf{c}(t)) . \tag{21}$$

Clearly, if we multiply (19) by c_j and integrate over $d^N c$, we get

$$\frac{d}{dt}\langle c_i\rangle=\langle K_i^{(1)\infty}(\mathbf{c})\rangle , \tag{22}$$

where $\langle\ \rangle$ denotes averaging with respect to P_∞. Since (20) holds, Eqs. (21) and (22) are identical. Thus the macroscopic limit yields a deterministic, macrovariable equation. In constructing the master equation for a particular macrovariable dynamics, the goal is to have (21) be identical with the original macrovariable dynamics. Mathematically, there are many W's which can do this, and which one is correct must be decided by the mesoscopic physics underlying the macrovariable equation.

We can also obtain the fluctuations around the deterministic dynamics in (21) by further analysis of the Kramers-Moyal equation (18).[10,15,17] We introduce the scaled deviations $\boldsymbol{\mu}$ (fluctuations) from the deterministic motion $\mathbf{c}(t)$ defined by

$$c_i=c_i(t)+\Omega^{-1/2}\mu_i . \tag{23}$$

Using (21) and replacing $\mathbf{c}$ in (18) by (23) and then Taylor-expanding all functions with respect to $\boldsymbol{\mu}$, yields and equation for the distribution of the fluctuations, $\phi(\boldsymbol{\mu},t)$:

$$\frac{\partial}{\partial t}\phi(\boldsymbol{\mu},t)=-\frac{\partial}{\partial\mu_i}\left[\frac{\partial}{\partial c_j}K_i^{(1)\infty}(\mathbf{c}(t))\mu_j\phi(\boldsymbol{\mu},t)\right] +\frac{1}{2}\frac{\partial^2}{\partial\mu_i\partial\mu_j}R_{ij}^{(2)}(\mathbf{c}(t))\phi(\boldsymbol{\mu},t) , \tag{24}$$

in which $R^{(2)}$ is defined by

$$R_{ij}^{(2)}=\lim_{\Omega\to\infty}\Omega K_{ij}^{(2)}(\mathbf{c}(t)) . \tag{25}$$

Both $K^{(1)\infty}$ and $R^{(2)}$ depend on the determination trajectory, $\mathbf{c}(t)$, determined by (21). In fact, the coefficients of the μ terms in the first part of the right-hand side of (24) (the "streaming term") are precisely the Jacobi matrix for (21):

$$J_{ij}=\frac{\partial K_i^{(1)\infty}}{\partial c_j} . \tag{26}$$

Introduce the covariance matrix C_{ij} defined by

$$C_{ij}=\langle\mu_i\mu_j\rangle , \tag{27}$$

in which $\langle\ \rangle$ now denotes averaging with respect to $\phi(\boldsymbol{\mu},t)$. Equation (24) may be used to prove that C_{ij} satisfies the equation[7]

$$\frac{d}{dt}C_{ij}=J_{ik}C_{kj}+C_{ik}J_{jk}+R_{ij}^{(2)} . \tag{28}$$

Thus, not only does J_{ij} govern the determination of the Liapunov exponent for the deterministic macrovariable equation (21), but it also governs the evolution of the fluctuation covariance matrix through Eq. (28). J_{ij} inherits time dependence from (21) through its explicit dependence on $\mathbf{c}(t)$.

Normally, the dynamics begins with some precise initial state, $\mathbf{c}(0)$ and no initial covariances, $C_{ij}(0)=0$. The $R_{ij}^{(2)}$ term in (28) drives the growth of a nonzero C_{ij}.

Keizer and Tilden[18] studied the growth of C_{ij} for simple limit cycles and for chaotic trajectories generated by the Rossler model.[19] Their numerical studies showed that for a chaotic trajectory, C_{ij} grew exponentially at a rate that appeared to be twice the Liapunov exponent for that trajectory. We have recently proved that this observation is not an accident.[20]

Equation (28) may be considered to be an equation for the evolution of the "vector" C_{ij}. Consider the metric for this space defined by

$$\|C\|=(\mathrm{tr}C^2)^{1/2} . \tag{29}$$

The corresponding Liapunov exponent λ_C is defined by

$$\lambda_C=\lim_{\substack{t\to\infty \\ \mathrm{tr}C^2(0)\to 0}}\frac{1}{t}\ln\left[\frac{[\mathrm{tr}C^2(t)]^{1/2}}{[\mathrm{tr}C^2(0)]^{1/2}}\right] . \tag{30}$$

On account of the common role of J_{ij} for both λ and λ_C, we were able to prove[20]

$$\lambda_C = 2\lambda \ , \tag{31}$$

in which λ is the Liapunov exponent for the dynamics given in (21), and for which λ is defined as in (5).

Before proceeding to the radical consequences of the exponential growth of the covariance matrix for a chaotic macrovariable trajectory, it is important to emphasize the two distinct ways in which we use Eq. (28). For nonchaotic trajectories, that approach stable steady states, the covariance matrix elments remain very small [of order unity for the scaling in (23), which means that the unscaled covariance matrix elements are of order $1/\Omega$], and represent the physically real fluctuations "carried on the back" of the deterministic motion.[7] However, for the chaotic trajectories, for which the covariance matrix elements diverge exponentially, we no longer view them as physically correct since they ultimately grow much too large, and because their origin is in Eq. (24), which followed from (18), provided they are *not* too large. Nevertheless, we have found that Eq. (28) may be used as a purely mathematical device for computing the Liapunov exponent. Thus we have used it to compute Liapunov exponents for the Rossler and Lorenz models[21] and have obtained three-decimal-place agreement with standard methods.[1] Moreover, when (28) implies that the covariance matrix elements diverge for a chaotic trajectory, the real physical fluctuations do indeed grow very large. While (28) is not an accurate way to handle large physical fluctuations, the underlying master equation (14) still is. Therefore we use (28) to compute λ, but we revert to (14) to do the physical treatment of the dynamics.

The radical consequence of chaos for the macrovariable dynamics is that the justification for the macrovariable equation (21) from the underlying master equation (14) breaks down. The reason for this breakdown is that the Dirac δ function solution to (19) given in (20) is not a stable solution to (19). The slightest bit of width added to the Dirac δ distribution leads to exponentially growing covariance matrix elements. Thus any initial distribution other than $P_\infty(\mathbf{c},0)=\delta(\mathbf{c}-\mathbf{c}(0))$ will not evolve like the expression in (20). Consequently, (22) will not reduce to (21) since the average of nonlinear terms such as $\langle K_i^{(1)\infty}(\mathbf{c})\rangle$ does not reduce to the nonlinear functions of the averages $K_i^{(1)\infty}(\langle \mathbf{c}\rangle)$. Simply put, the contraction of the master equation into a deterministic macrovariable equation does not occur. A proper description of the dynamics and its associated, large scale fluctuations must be done at the mesoscopic level of the master equation.

There are several picturesque ways of expressing this result for more specific situations. For example, when the Navier-Stokes equations (hydrodynamics) predict chaos (numerically[22] they are certainly able to do so), the Navier-Stokes equations are no longer valid; or, you cannot get a theory of turbulence from Navier-Stokes alone. Similarly, when the mass action chemical reaction equations imply chaos (numerically), these equations are physically invalid.

There is an important provision to this conclusion and each of its particular realizations. The invalidity of the Dirac δ function solution to (19) which is at the core of our results reflects its instability with respect to any sort of initial probability distribution width. Nevertheless, if the initial width is very small and the Liapunov exponent for the chaotic trajectory is also very small, the instability may take a very long time to manifest itself. Thus the Dirac δ function solution may prove to be a very good approximation over a time interval which is longer than the time taken to do the associated experiment. For example, one may say that Navier-Stokes will work well, for a while, in the case of "weak" turbulence. Clearly, for any given situation, one must determine the Liapunov exponent and size of the initial width in the distribution [this is determined by $R^{(2)}(0)$], in order to decide whether or not to discard the macrovariable equations in favor of the master equation.

Detailed accounts of these phenomena for the Rossler model, the Lorenz model,[23] and the periodically driven Brussellator[24] (a particular chemical reaction with a cubic nonlinearity) may be found in a forthcoming paper coauthored with Keizer, Tilden, and Fox.[20]

III. THE CORRESPONDENCE LIMIT

In Sec. I we showed that there are two equivalent ways to describe the time evolution of an N variable dynamical system. Either N coupled first order, ordinary differential equations are used to determine the unique N variable trajectories, or an $N+1$ variable (N x_i's and t) partial differential equation, the Liouville equation for the conserved probability, is used to obtain a Dirac δ function solution that follows precisely the N variable trajectory. In classical mechanics, these two alternatives also exist, although now we have $2N$ coupled, ordinary differential equations for N coordinates and their N conjugate momenta, or a $2N+1$ variable partial differential equation, Liouville's equation. A quite general treatment of the correspondence limit for the relationship between quantum mechanics and classical mechanics can be developed if we focus on the Liouville equation.

In 1932, Wigner published a paper[25] aimed at obtaining quantum corrections to formulas for thermodynamic equilibrium. In doing so, he formulated a quantum-mechanical generalization of Liouville's equation that becomes Liouville's equation in the correspondence limit (i.e., as $\hbar \to 0$). The remarkable feature of this correspondence limit which we will exploit here is that it is formally isomorphic to the connection between the master equation and the macrovariable equations, specifically to the connection between (18) and (19). Moreover, by applying the same procedure[10,15,17] to get from (18) to (24), we can also obtain an equation for the fluctuations associated with the Wigner-Liouville connection. Throughout this presentation the role of Ω^{-1} is played by $\hbar$, and naturally $\Omega \to \infty$ corresponds with $\hbar \to 0$. The consequences of these considerations for the correspondence limit when the classical dynamics is strongly chaotic are radical.

Consider the Hamiltonian

$$H = \sum_{k=1}^{n} \frac{p_k^2}{2m_k} + V(x_1 x_2 \cdots x_n) \ . \tag{32}$$

The Wigner distribution for this n-coordinated system is defined[25] by

$$W(x_1 \cdots x_n p_1 \cdots p_n) = \left[\frac{1}{\pi\hbar}\right]^n \int \cdots \int dy_1 \cdots dy_n \psi^*(x_1+y_1 \cdots x_n+y_n)\psi(x_1-y_1 \cdots x_n-y_n) \times \exp\left[2\frac{i}{\hbar}(p_1 y_1 + \cdots + p_n y_n)\right], \tag{33}$$

in which the p_i's are ordinary parameters rather than differential operators as in the quantum interpretation of (32). W is not a probability distribution because it is sometimes negative. However, both of its reduced distributions are the correct probability distributions,[25] as is easily proved: $\int \cdots \int dp_1 \cdots dp_n W$ is the probability distribution for the x_i's and $\int \cdots \int dx_1 \cdots dx_n W$ is the probability distribution for the p_i's. Wigner showed[25] that the time evolution of W is given by

$$\frac{\partial}{\partial t}W = -\frac{p_k}{m_k}\frac{\partial}{\partial x_k}W + \left[\frac{\partial}{\partial x_k}V\right]\frac{\partial}{\partial p_k}W + \sum_{\substack{\lambda_1+\cdots+\lambda_n \\ \text{odd}}} \left[\frac{\partial^{\lambda_1+\cdots+\lambda_n}}{\partial_{x_1}^{\lambda_1}\cdots\partial_{x_n}^{\lambda_n}}V\right] \frac{\left[\frac{\hbar}{2i}\right]^{\lambda_1+\cdots+\lambda_n-1}}{\lambda_1!\cdots\lambda_n!} \frac{\partial^{\lambda_1+\cdots+\lambda_n}}{\partial_{p_1}^{\lambda_1}\cdots\partial_{p_n}^{\lambda_n}}W , \tag{34}$$

in which the second line is a summation over all $\lambda_1+\cdots+\lambda_n$ that are odd. The remarkable features of this equation are that the $\hbar$-independent terms are identical with Liouville's equation for Hamiltonian (32) treated classically, and the remaining terms are at least of order $\hbar^2$ and contain at least the third derivative of the potential, V. This is the equation that parallels the Kramers-Moyal equation (18) with $\hbar$ in the role of Ω^{-1}. Clearly, all that remains, if $\hbar \to 0$, is the classical Liouville equation, that parallels Eq. (19). It has a Dirac δ function solution that follows the solution to Hamilton's equations of motion:

$$\frac{d}{dt}x_i(t) = \frac{p_i(t)}{m_i} , \tag{35}$$

$$\frac{d}{dt}p_i(t) = -\frac{\partial}{\partial x_i}V(x_1(t)\cdots x_n(t)) . \tag{36}$$

In parallel with our treatment of macrovariable fluctuations, Eq. (34) may be analyzed[10,15,17] to determine the quantum fluctuations attending the classical motion. We introduce the scaled deviations, μ_i and q_i, (fluctuations) from the classical motion, $x_i(t)$ and $p_i(t)$, defined by

$$x_i = x_i(t) + \hbar^{1/2}\mu_i , \tag{37}$$

$$p_i = p_i(t) + \hbar^{1/2}q_i . \tag{38}$$

Replacing x_i and p_i in (34) by (37) and (38), and Taylor-expanding V with respect to the μ_i's eventually yields an equation for the distribution of the fluctuations, $\phi(\boldsymbol{\mu},\mathbf{q},t)$:

$$\frac{\partial}{\partial t}\phi(\boldsymbol{\mu},\mathbf{q},t) = -\frac{q_k}{m_k}\frac{\partial}{\partial \mu_k}\phi(\boldsymbol{\mu},\mathbf{q},t) + \left[\frac{\partial^2}{\partial x_j \partial x_k}V\right]\mu_j\frac{\partial}{\partial q_k}\phi(\boldsymbol{\mu},\mathbf{q},t) + O(h^{1/2}) . \tag{39}$$

In order to satisfy Heisenberg's uncertainty principle, this equation must have the initial distribution (for minimum uncertainty) given by

$$\phi(\boldsymbol{\mu},\mathbf{q},t) = \prod_{j=1}^{n}\frac{1}{4\pi}\exp\left[-\frac{\mu_j^2}{2\sigma^2} - 2\sigma^2 q_j^2\right] \tag{40}$$

so that

$$[\langle(\Delta\mu_i)^2\rangle]^{1/2}[\langle(\Delta q_i)^2\rangle]^{1/2} = \sigma\frac{1}{2\sigma} = \frac{1}{2} , \tag{41}$$

which is the scaled version [see (37) and (38)] of the Heisenberg uncertainty requirement. Notice that, unlike (24), Eq. (39) contains no second-order derivatives in μ_i's or q_i's, i.e., no terms like the $R^{(2)}$ terms in (24). This fact reflects the intrinsic difference between macrovariable equations described by either (1) or (14) which are *dissipative*, and Hamiltonian equations described by either (34) or (35) and (36) which are *conservative*. The diffusive $R^{(2)}$ term in (24) also shows up in the covariance equation (28). We will now turn to the analog of (28) for the present case.

Let z_i for $i = 1,2,\ldots,2n$ be defined by

$$z_1 = x_i, \quad i = 1,2,\ldots,n \tag{42}$$

and

$$z_i = p_{i-n}, \quad i = n+1, n+2, \ldots, 2n . \tag{43}$$

Hamilton's equations (35) and (36) may be written in the form

$$\dot{x}_i = \frac{\partial H}{\partial p_i} , \tag{44}$$

$$\dot{p}_i = -\frac{\partial H}{\partial x_i} . \tag{45}$$

Let the $2n \times 2n$ matrix $\underline{I}$ be defined by

$$\underline{I} = \begin{bmatrix} \underline{0} & \underline{E} \\ -\underline{E} & \underline{0} \end{bmatrix} , \tag{46}$$

in which $\underline{0}$ is the $n\times n$ zero matrix and $\underline{E}$ is the $n\times n$ identity matrix. With $\underline{I}$, Eqs. (44) and (45) may be rewritten in the form

$$\dot{z}_i = I_{ij}\frac{\partial H}{\partial z_j} \ . \tag{47}$$

(I_{ij} reflects the so-called symplectic structure[26] of Hamiltonian dynamics.) The Jacobi matrix J_{ij} for this dynamics is just

$$J_{ij} = I_{ik}\frac{\partial^2 H}{\partial z_j \partial z_k} \ , \tag{48}$$

a $2n\times 2n$ matrix. Now, let η_i be defined by

$$z_i = z_i(t) + \hbar^{1/2}\eta_i \ , \tag{49}$$

i.e.,

$$\eta_i = \mu_i, \quad i = 1,2,\ldots,n \tag{50}$$

$$\eta_i = q_{i-n}, \quad i = n+1, n+2, \ldots, 2n \ . \tag{51}$$

Therefore (39) becomes

$$\frac{\partial}{\partial t}\phi(\boldsymbol{\eta},t) = -J_{ij}\eta_i\frac{\partial}{\partial \eta_j}\phi(\boldsymbol{\eta},t) \ , \tag{52}$$

which has precisely the same form as the streaming term in (24).

Let the covariance matrix C_{ij} be defined by

$$C_{ij} = \langle \eta_i \eta_j \rangle \ , \tag{53}$$

in which $\langle\ \rangle$ defined averaging with respect to $\phi(\boldsymbol{\eta},t)$. Equation (52) implies

$$\frac{d}{dt}C_{ij} = J_{ik}C_{kj} + C_{ik}J_{jk} \tag{54}$$

and (40) implies the initial conditions for C_{ij} given by

$$C_{ij} = \sigma^2\delta_{ij}, \quad i,j = 1,2,\ldots,n \tag{55}$$

$$C_{ij} = \frac{1}{4\sigma^2}\delta_{ij}, \quad i,j = n+1, n+2, \ldots, 2n \tag{56}$$

$$C_{ij} = 0 \quad \text{otherwise} \ . \tag{57}$$

This differs from (28) since there is no $R^{(2)}$ inhomogeneity. However, for (28) the initial condition on the covariance matrix was that it vanished, and $R^{(2)}$ causes it to become nonzero, reflecting the underlying fluctuation-dissipation relation.[5,7,15] In (54), there is no $R^{(2)}$ term because the underlying dynamics is conservative, but Heisenberg's uncertainty principle requires the initial C_{ij} to be nonzero. Nevertheless, just as with (28), this equation has a Liapunov exponent defined by (30) and satisfying identity (31) where this time λ is the largest positive Liapunov exponent implied by the classical dynamics (47) and governed by the Jacobi matrix (48). This, of course, means that if the classical trajectory is chaotic ($\lambda > 0$), then the covariance matrix will diverge, or, in other words, the quantum fluctuations become macroscopically large.

The correspondence limit applies when a classical-mechanical motion is described using the underlying quantum mechanics. The correspondence limit is verified when one shows that the quantum-mechanical treatment yields the classical motion plus ignorable quantum corrections. As we have shown above, a minimum uncertainty distribution can be chosen so that the coordinates have a very small quantum variance, i.e., σ may be taken to be very small. However, this implies that the covariance for the conjugate momenta goes like $1/2\sigma$. If the expectation values for the momenta are "classical," then it is still possible to have the variances $1/2\sigma$ be very small *compared* to the expectations. This is the essence of the classical correspondence limit for the quantum dynamics. (We may also consider the situation in which the roles of coordinates and momenta are reversed.) Using the Wigner distribution, we see that these conditions translate into Liouville's equation, the classical limit of (34), along with an initial distribution which is essentially a Dirac δ function, since its scaled representation is governed by the initial distribution for (39), i.e., (40), which is as narrow as one would like in both the coordinates (σ) and the conjugate momenta ($1/2\sigma$/momentum expectation value). As long as (39), or equivalently (54), implies that the covariances do not grow large, compared to the expectation values, this classical limit, the "correspondence" limit, is maintained. But chaos in the classical notion clearly invalidates this correspondence because the Jacobi matrix for the classical motion governs the growth of quantum fluctuations through Eq. (54) and creates a positive Liapunov exponent for the classical motion as well as for the covariance matrix equation. Thus, when the classical motion is chaotic, Liouville's equation does not have a Dirac δ function solution for all time. Its solution is not equivalent to Hamilton's equations of motion since averaging over its non-Dirac δ function solution will not reproduce Hamilton's equations [cf. (21) and (22)]. One must not attempt to contract the Wigner equation description in such a case. This means one must simply stay with the original Schrödinger equation for the entire description.

Even though the Schrödinger probability distribution can be made initially to be as sharp as one would like around the initial classical variables, strong chaos makes it grow broad rapidly. These remarks are entirely parallel to our earlier remarks regarding the master equation and the macrovariable equations and chaos. This also means there is an identical proviso, i.e., the need to use quantum mechanics for the description of a chaotic classical-mechanical motion depends on the initial size of the quantum fluctuations ($\hbar$ and σ) and on the size of λ. It is sometimes possible that the quantum fluctuations will not become too large to ignore on the time scale of the computation or experiment involved. One will need to ascertain by simulation whether or not chaos forces the abandonment of the classical description. Surely, chaotic classical motion in the Solar System[27] is an example where the quantum fluctuations may safely be ignored even on an "astronomical" time scale. For more down to Earth examples, the possibility of macroscopically large quantum fluctuations in an otherwise classical system is now seen to be a very real possibility. In parallel with our earlier picturesque statements for macrovariable

chaos, one may say that to properly describe classical-mechanical chaos, one must do quantum mechanics.

In a companion paper,[28] a detailed account of how the correspondence principle works for the nonchaotic or very weakly chaotic classical case, and then fails for the strongly chaotic case, is given for the periodically kicked pendulum. We have used extensive numerical computation to study the rapid growth of quantum fluctuations in this example when the classical dynamics is strongly chaotic.

IV. EXPERIMENTAL CONFIRMATION

There are two specific examples that may readily lead to experimental testing which we will now discuss. One is a macrovariable problem: hydrodynamic turbulence; and the other is an essentially quantum-classical correspondence problem: the laser. Our initial remarks apply to both cases.

There does not appear to be any reason to have to invent new kinds of experiments to test the ideas in this paper. Experimenters already use a statistical approach to these types of problems. There are a wide variety of techniques for measuring moments of variables, entire distribution functions, correlation functions and their power spectra, for doing light scattering, etc. With either a hydrodynamics paradigm or a laser paradigm, there is a set of deterministic equations which are used to model the physical system. These equations are usually deemed appropriate on the basis of equilibrium or steady-state measurements and computations. By obtaining parameter settings that make the solutions to the equations chaotic, the experimenter can attempt to arrange his apparatus settings to mimic the mathematical chaos. In reality, there are various sources of noise that make this comparison difficult. However, noise terms may be added to the equations used as a model and the influences of these noise terms can then be deduced by numerical simulation.[29] The basic point is that the predicted statistics for deterministic equations which include various noise terms (additive and/or multiplicative) are different from the predictions based upon an underlying master equation (or the underlying quantum mechanics). For example, if we add Gaussian fluctuations to Eq. (1), a Fokker-Planck equation can be derived in which the streaming term is governed by the F_i's. However, for chaos, if we take the view expressed in this paper, we must instead use the master equation underlying (1), and since (1) is no longer a valid contraction, the F_i's do not appear anywhere in this alternative description. We clearly get two distinct predictions.

Hydrodynamics presents an extra difficulty to which we alluded in Sec. II. There is as yet no accepted underlying master equation. This can probably be attributed to a combination of the intrinsic difficulty in obtaining one and, till now, not having any compelling reason to construct one.[7,30] Nevertheless, the Navier-Stokes equations produce numerical chaos,[22] and to date no one has been able to claim quantitative agreement between numerical work and physical measurements. The situation is very much better for nonchaotic hydrodynamic states created in the Benard system and in the Taylor-Couette system.[31] The agreement between Navier-Stokes and measurements is then excellent.

The laser problem not only involves the quantum-classical correspondence but also has the character of a macrovariable problem. This is a consequence of using a few, highly contracted, variables to treat the laser, rather than the full density matrix.[32] By now, it is very evident that these equations do not adequately model the behavior of real lasers when the lasers are operated under conditions which the laser equations predict lead to strong chaos.[33] Clearly, one should attempt to do a much better mesoscopic, or even full density matrix, modeling job. The quantum fluctuations have become so large that the contraction down to simple semiclassical equations in terms of intensities and molecular state populations is invalid. Nevertheless, the measurements already undertaken are probably adequate to test these ideas; it is the correct mesoscopic description and treatment which is presently lacking.

Another experimental paradigm for the study of large quantum fluctuations may be the Josephson junction. Its behavior can be treated as a periodically modulated damped pendulum.[34] The Wigner-Liouville correspondence analysis of Sec. III is easily applied to this concrete case in the undamped case. The damping may present an unfortunate difficulty, however.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grant No. PHY-8902549. Part of this work was done at the Institute for Theoretical Dynamics at the University of California at Davis, in close collaboration with Joel Keizer. The correspondence limit work has been done in part with B. L. Lan, and has benefited from numerous discussions with Joseph Ford.

[1]A. J. Lichtenberg and M. A. Lieberman, *Regular and Stochastic Motion* (Springer-Verlag, New York, 1983), Sec. 5.2b.

[2]L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959).

[3]G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, RI, 1963), Chap. VII.

[4]D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin/Cummings, Reading, MA, 1975).

[5]R. F. Fox and G. E. Uhlenbeck, Phys. Fluids **13**, 1893 (1970); **13**, 2881 (1970).

[6]B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

[7]J. E. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes* (Springer-Verlag, New York, 1987).

[8]D. A. McQuarrie, J. Appl. Prob. **4**, 413 (1967).

[9]T. G. Kurtz, J. Appl. Prob. **7**, 49 (1970); **8**, 344 (1971).

[10]N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981), Chap. V.
[11]R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975), Sec. 20.4.
[12]J. A. McLennon, *Introduction to Nonequilibrium Statistical Mechanics* (Prentice Hall, Englewood Cliffs, NJ, 1989), Chap. 7.
[13]H. A. Kramers, Physica **7**, 284 (1940).
[14]J. E. Moyal, J. R. Stat. Soc. B **11**, 150 (1949).
[15]R. F. Fox, Phys. Rep. **48**, 179 (1978), Sec. I.5.
[16]N. G. van Kampen, Can. J. Phys. **39**, 551 (1961).
[17]R. Kubo, K. Matsuo, and K. Kitahara, J. Stat. Phys. **9**, 51 (1973).
[18]J. E. Keizer and J. Tilden, J. Chem. Phys. **93**, 2811 (1989).
[19]A. J. Lichtenberg and M. A. Lieberman, Ref. 1, Sec. 7.1b.
[20]J. E. Keizer, J. Tilden, and R. F. Fox (unpublished).
[21]A. J. Lichtenberg and M. A. Lieberman, Ref. 1, Sec. 7.4a.
[22]R. G. Deissler, NASA Technical Memorandum No. 101983, 1989 (unpublished).
[23]E. N. Lorenz, J. Atmos. Sci. **20**, 130 (1963).
[24]K. Tomita, Phys. Rep. **86** (1982).
[25]E. Wigner, Phys. Rev. **40**, 749 (1932).
[26]V. I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer-Verlag, New York, 1978), Chap. 8.
[27]J. Wisdom, Proc. R. Soc. London, Ser. A **413**, 109 (1987); Icarus **72**, 241 (1987).
[28]R. F. Fox and B. L. Lan, preceding paper, Phys. Rev. A **41**, 2952 (1990).
[29]S. Zhu, A. W. Yu, and R. Roy, Phys. Rev. A **34**, 4333 (1986).
[30]N. G. van Kampen, Ref. 10, Chap. XII.
[31]H. L. Swinney, Physica **7D**, 3 (1983).
[32]M. Sargent, M. O. Scully, and W. E. Lamb, *Laser Physics* (Addison-Wesley, Reading, MA, 1974).
[33]E. Arimondo (private communication).
[34]P. Bak, T. Bohr, M. H. Jensen, and P. V. Christiansen, Solid State Commun. **51**, 231 (1984).