Lyapunov Spectra, Instantaneous Normal Mode Spectra, and Relaxation in the Lennard-Jones Liquid

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Lyapunov spectra are obtained numerically for the Lennard-Jones liquid for a range of temperatures. An approximation scheme for calculating the Lyapunov spectrum is described, assuming knowledge of (i) the instantaneous normal mode spectrum which characterizes the local potential energy landscape, and (ii) a decorrelation time. The adaptation, for this purpose, of an analytical relation by Newman is described. The temperature dependence of the maximum Lyapunov exponent, calculated with an *ansatz* for the decorrelation time, is shown to be in excellent agreement with simulation results. [S0031-9007(96)00182-2]

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Chaotic dynamics in classical many body systems has increasingly come under study in research aimed at characterizing macroscopic behavior in terms of fundamental microscopic dynamics [1–3]. In particular, considerable progress has recently been made in calculating transport coefficients by analyzing the chaotic dynamics in classical fluids [1,2]. Among the principal quantities of interest in studying chaotic dynamics are the Lyapunov exponents, which quantify the exponential separation of nearby trajectories in a chaotic system. For systems with many degrees of freedom, however, the calculation of Lyapunov exponents is challenging, both analytically and in simulation. Few analytical schemes exist for such calculations. Although reliable simulation methods exist, the computational expense is by no means trivial if one wishes to calculate all the Lyapunov exponents, i.e., the Lyapunov spectrum, in a many body system. Methods for calculating the Lyapunov spectrum by means other than direct simulation are thus of considerable interest. Such a method is presented in this Letter, wherein the Lyapunov spectrum for the Lennard-Jones liquid is calculated from the knowledge of its average potential energy landscape. The Lyapunov spectra calculated thus are compared with spectra obtained from simulations.

The multidimensional potential energy landscape has recently been studied for a variety of systems [4–7], with the aim of elucidating a range of macroscopic dynamical phenomena. The *local* potential energy landscape is characterized by the "instantaneous normal mode" (INM) spectrum [5,6]. The average potential energy landscape, and hence the INM spectrum, depends on the equilibrium sampling of configurations, which is determined by system parameters such as temperature and density. The INM spectrum is obtained as the equilibrium ensemble average over configurations of the square roots of curvatures of the potential energy surface [i.e., eigenvalues of the matrix of potential energy second derivatives (Hessian)] defined at a given configuration. Thus, the INM spectrum is an *equilibrium* property of the system, which may be calculated in principle by the methods of equilibrium statistical mechanics. Indeed, such a calculation, starting from the interaction potential, has substantially been accomplished for simple liquids [6]. The INM spectrum of a liquid in general has both real and imaginary frequencies, since typical configurations of a liquid are not in mechanical equilibrium.

The time evolution of infinitesimal displacements from the reference trajectory, from which Lyapunov exponents are calculated, is governed by the Hessian matrix evaluated along the reference trajectory. The full spectrum of Lyapunov exponents may be calculated from the eigenvalues of the $6N \times 6N$ (N is the number of atoms) dynamical matrix $\mathbf{S}(t)$, whose time evolution is given by

$$\dot{\mathbf{S}}(t) = \begin{pmatrix} \mathbf{0} & \mathbf{1} \\ -\mathbf{V}''(t) & \mathbf{0} \end{pmatrix} \mathbf{S}(t), \qquad \mathbf{V}''(t) = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right), \tag{1}$$

where $\mathbf{V}''(t)$ is the time dependent Hessian matrix, $\mathbf{1}$ and $\mathbf{0}$ represent $3N \times 3N$ unit and null matrices. The first (second) $3N$ rows of $\mathbf{S}(t)$ contain position (momentum) coordinates q (p). Note that $\mathbf{S}(t)$ depends nontrivially only on $\mathbf{V}''(t)$. If $\sigma_j(t), j = \{1, 2, \ldots, 6N\}$ are the eigenvalues of $[\mathbf{S}(t)^T \cdot \mathbf{S}(t)]^{1/2}$, the Lyapunov exponents λ_j are given by $\lambda_j = \lim_{t\to\infty}(1/t)\ln\sigma_j$.

I first calculate Lyapunov spectra in standard classical molecular dynamics simulations [8], using the numerical procedure suggested by Eckmann and Ruelle [9] for a system of 32 atoms interacting via the Lennard-Jones potential, at reduced density $\rho^* = 1$, for a range of temperatures from $T^* = 0.401$ to 6.808. Plotting $j/6N$ as a function of λ_j (arranged in increasing order) one gets the cumulative Lyapunov spectrum $H(\lambda)$, $dH(\lambda)/d\lambda \equiv L(\lambda)$ being the spectral density or the Lyapunov spectrum. In conservative Hamiltonian systems, the Lyapunov exponents come in conjugate pairs, each of which add to zero [10], and thus $H(\lambda) = 1 - H(-\lambda)$. The cumulative

spectrum is shown for $T^* = 1.271$ in Fig. 1 (the spectrum is shown only for negative exponents exploiting the above mentioned symmetry). For the entire range of temperatures studied, I find that $H(\lambda)$ can be fit very well by the form

$$H(\lambda) = \frac{1}{2}\left(1 + \frac{\arctan(\theta\lambda)}{\arctan(\theta\lambda_{\max})}\right), \qquad (2)$$

corresponding to a Lorenzian Lyapunov spectrum $L(\lambda)$ in the scaled variable $(\theta\lambda)$, for $-\lambda_{\max} \le \lambda \le \lambda_{\max}$. The temperature dependence of $\lambda_{\max}$ is shown in Fig. 2 (the theoretical calculation shown in Fig. 2 is discussed later). The inverse width of the Lorenzian, θ, is a decreasing function of temperature, varying roughly as T^{*-1} (data not shown). This generic form of the spectra is different from those proposed in, e.g., [11]. A detailed discussion of the form of Lyapunov spectra is deferred to a future publication.

I now develop an approximation scheme (along similar lines to Ref. [12]) for calculating the Lyapunov spectrum in terms of the INM spectrum. For large N, the eigenvalues of $\mathbf{V}''(t)$ may be expected (and assumed from here on) not to change with t. The eigenvectors, however, do change and contain all the nontrivial information regarding the time dependence of $\mathbf{S}(t)$ if the INM spectrum is known. If it is assumed that a time scale τ can be identified over which the eigenvectors become completely decorrelated from their initial state (i.e., assume a simple relaxation behavior), then with the specific model of this relaxation which assumes that the eigenvectors (i) remain fixed for intervals $[(i-1)\tau, i\tau]$, $i = 1, 2, \ldots$, and (ii) are uncorrelated between successive intervals, the expression in Eq. (1) for $\mathbf{S}(t)$ at $t = n\tau$ simplifies to

$$\mathbf{S}(n\tau) = \prod_{i=0}^{n} \mathbf{S}_i\,, \qquad (3)$$

where $\mathbf{S}_i$ are obtained by integrating Eq. (1) between $t = (i-1)\tau$ and $t = i\tau$. Let γ_j be the eigenvalues of $\mathbf{V}''$ and $\omega_j = |\gamma_j|^{(1/2)}$. Defining $C(\omega_j, \tau) \equiv \cos(\omega_j\tau)$ and $S(\omega_j, \tau) \equiv \sin(\omega_j\tau)$ if $\gamma_j > 0$, $C(\omega_j, \tau) \equiv \cosh(\omega_j\tau)$ and $S(\omega_j, \tau) \equiv \sinh(\omega_j\tau)$ if $\gamma_j < 0$, integrating Eq. (1) between $t = (i-1)\tau$ and $t = i\tau$ leads to the explicit expression of $\mathbf{S}_i$,

$$\mathbf{S}_i = \begin{pmatrix} \mathbf{N}_i & \mathbf{0} \\ \mathbf{0} & \mathbf{N}_i \end{pmatrix} \begin{pmatrix} \boldsymbol{C} & \boldsymbol{S_1} \\ \boldsymbol{S_2} & \boldsymbol{C} \end{pmatrix} \begin{pmatrix} \mathbf{N}_i^T & \mathbf{0} \\ \mathbf{0} & \mathbf{N}_i^T \end{pmatrix}, \qquad (4)$$

where $\mathbf{N}_i$ is the random $3N \times 3N$ orthogonal matrix defining the basis of $\mathbf{V}''$ for $[(i-1)\tau, i\tau]$, $\boldsymbol{C}_{k,l} = C(\omega_k, \tau)\delta_{k,l}$, $\boldsymbol{S}_{1_{k,l}} = (1/\omega_k)S(\omega_k, \tau)\delta_{k,l}$, and $\boldsymbol{S}_{2_{k,l}} = \mp\omega_k S(\omega_k, \tau)\delta_{k,l}$ [where the $-(+)$ applies when $\gamma_k > (<)\ 0$). The model of relaxation for the eigenvectors is crude, but it allows $\mathbf{S}(n\ \tau)$ to be calculated in terms of (i) the INM spectrum, (ii) the decorrelation time τ, and (iii) a statistical description of the eigenvectors.

Under these assumptions, I first calculate Lyapunov spectra numerically, by (i) using INM spectra obtained from simulations to define a fixed set of eigenvalues of $\mathbf{V}''$, (ii) generating random "eigenvectors" of $\mathbf{V}''$ [13] for successive time intervals, and (iii) specifying a decorrelation time τ. For all studied values of T and τ (above a lower cutoff), Eq. (2) describes the resulting $H(\lambda)$ well, with θ and $\lambda_{\max}$ increasing with τ. $H(\lambda)$ for $T^* = 1.271$ and $\tau = 0.225$ is shown in Fig. 1. While $\lambda_{\max}$ is seen to be close to the simulation value, the

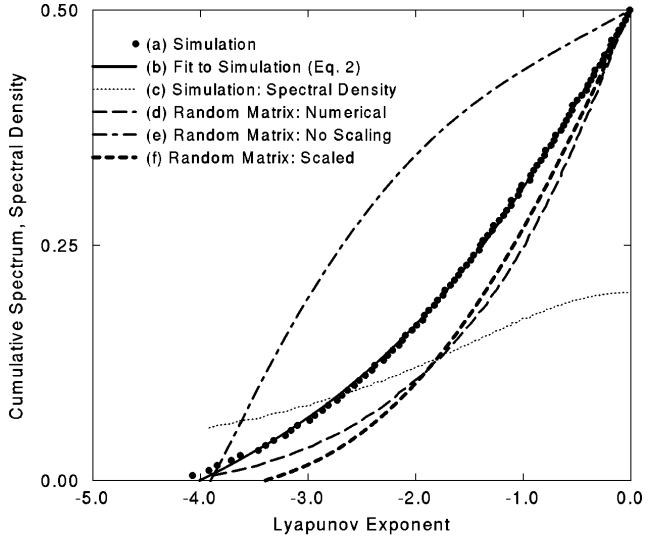

FIG. 1. Cumulative Lyapunov spectra for $T^* = 1.271$ (a) obtained in simulation. (b) Fit [Eq. (2)] to simulation spectrum in (a). (c) Spectral density from fit (b). Cumulative spectra in the random matrix approximation with $\tau = 0.225$: (d) Numerical evaluation. (e) Calculated from Eq. (5) without scaling (p, q) vector elements. (Note that the Lyapunov exponent values in this case have been divided by 3 to bring them into the same range as the rest.) (f) calculated from Eq. (5) after scaling (p, q) vector elements with scale factor η [Eq. (9)].

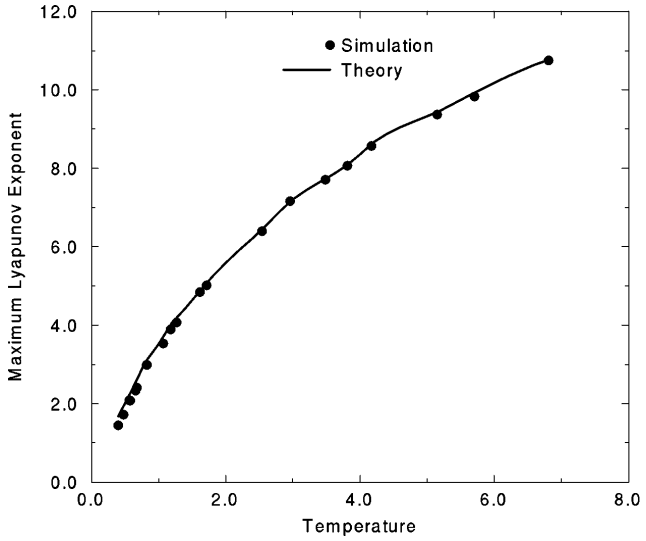

FIG. 2. The maximum Lyapunov exponent as a function of temperature from simulation, and as calculated from the empirical form for the INM spectrum and the *ansatz* for the decorrelation time, $\tau = 1.79/|\omega_u(T)|$.

inverse width θ is higher. In general, while a choice of τ can be found (for a given T^*) which leads to a reasonable approximation to the simulation spectrum (or $\lambda_{\max}$, θ individually), exact agreement for both $\lambda_{\max}$ and θ is not found for any τ.

Under the assumptions made above for $\mathbf{S}(t)$, and the assumption that vectors $\tilde{x}_j \equiv x_j/|x_j|$ (where $x_j = \prod_{i=0}^{j} S_i x_0$, for arbitrary x_0) have an invariant uniform distribution, Eckmann and Wayne [12] argued that an analytical result due to Newman [14] for calculating the Lyapunov spectrum of a product of random matrices may be applied to Hamiltonian systems. Considering matrices A_i such that $A_i^T\ A_i$ is equidistributed with OD^2O^T (where D is diagonal and O are orthogonal matrices whose columns are uniformly distributed) and assuming that a nonrandom asymptotic (as matrix size $\to \infty$) spectrum $K(\sigma)$ of eigenvalues of $(A_i^T\ A_i)^{(1/2)}$ exists, Newman [14] showed that $H(\lambda)$ is given by

$$\int \frac{\sigma^2 K(\sigma)\, d\sigma}{H(\lambda)\exp(2\lambda) + [1 - H(\lambda)]\sigma^2} = 1\,, \qquad (5)$$

for $\lambda \le \lambda_{\max}$, where

$$\lambda_{\max} = \frac{1}{2}\log\left(\int \sigma^2 K(\sigma)\, d\sigma\right). \qquad (6)$$

The eigenvalues of $(\mathbf{S}_i^T\ \mathbf{S}_i)$, with $\mathbf{S}_i$ as in Eq. (4), are

$$\sigma_{j\pm}^2 = \mathcal{E}(\omega_j,\tau) \pm [\mathcal{E}(\omega_j,\tau)^2 - 1]^{(1/2)}, \qquad (7)$$

where $\mathcal{E}(\omega,\tau) = C(\omega,\tau)^2 + A(\omega)S(\omega,\tau)^2$ and $A(\omega) = (\omega^{-2} + \omega^2)$. $K(\sigma)$ is the distribution of σ_j's. If applicable, Eq. (5) provides an analytical expression for the cumulative Lyapunov spectrum in terms of the INM spectrum, under the stated approximations. However, when Eq. (5) is used to calculate $H(\lambda)$, the result is in glaring disagreement with both the simulation and the numerical random matrix calculation, in both the shape of the spectrum and the range of λ values. An example is shown in Fig. 1 for $T^* = 1.271$ and $\tau = 0.225$ (note that λ values for this case have been divided by 3 in the graph). Such disagreement is found for all the T^* and τ values studied. Hence the applicability of Eq. (5) to the present problem needs reexamination.

The assumption of a uniform, invariant distribution for $\tilde{x}_j$ turns out not to be valid for Hamiltonian systems, as was suspected in [12]. This can be demonstrated by considering the distribution of elements of vectors $\tilde{x}_j$. For large N, if $\tilde{x}_j$ has a uniform distribution, the individual elements of $\tilde{x}_j$ have a Gaussian distribution with mean zero and a variance that is the same for all elements [15]. Calculating distributions for various q and p elements of vectors $\tilde{x}_j$ during the numerical evaluation of Lyapunov spectra, I find that for a given vector the distributions for q elements are different from those of p elements, but all q elements (and, all p elements) have the same *Gaussian* distribution. An example is shown in the inset of Fig. 3. The standard deviation of q elements σ_q (and σ_p) is a function of both T^* and τ. Figure 3 shows the variation of σ_q with τ for $T^* = 1.271$.

The calculation of $H(\lambda)$ can be recast in a form that makes Eq. (5) applicable by using a metric that imposes different scales (proportional to σ_q and σ_p) on the q and p subspaces. This is equivalent to reexpressing the matrices $\mathbf{S}_i$ by changing $\boldsymbol{S_1}$ to $\eta^{-1}\boldsymbol{S_1}$ and $\boldsymbol{S_2}$ to $\eta\boldsymbol{S_2}$ in Eq. (4), where $\eta = \sigma_q/\sigma_p$. The eigenvalues of $\mathbf{S}_i$ are still given by Eq. (7), but with $A(\omega) = (\eta\omega)^{-2} + (\eta\omega)^2$.

I calculate the scale factor η as follows. Considering normalized vectors $\tilde{x}_j = x_j/|x_j|, x_j = \prod_{i=0}^{j} S_i x_0$, and writing $\tilde{x}_j = \binom{\mathbf{q}_j}{\mathbf{p}_j}$, we have

$$\frac{|x_j|}{|x_{j-1}|}\begin{pmatrix}\mathbf{q}_j\\ \mathbf{p}_j\end{pmatrix} = \mathbf{S}_j\begin{pmatrix}\mathbf{q}_{j-1}\\ \mathbf{p}_{j-1}\end{pmatrix}, \qquad (8)$$

where $\mathbf{q}$ and $\mathbf{p}$ are vectors of length $3N$, and $\mathbf{S}_j$ is given by Eq. (4). For $N \to \infty$, the elements of $\mathbf{q}$, $\mathbf{p}$, and $\mathbf{N}_j$ can be written as $\mathbf{q}_{j_k} = \sigma_{q_j} n(0,1)$, $\mathbf{p}_{j_k} = \sigma_{p_j} n(0,1)$ [with the constraint $(3N)\,(\sigma_{q_j}^2 + \sigma_{p_j}^2) = 1$], and $\mathbf{N}_{j_{k,l}} = (1/\sqrt{3N})n(0,1)$, where $n(0,1)$ is a Gaussian random number with zero mean and unit variance. Demanding then that $\sigma_{q_j} = \sigma_{q_{j-1}} \equiv \sigma_q$, and $\sigma_{p_j} = \sigma_{p_{j-1}} \equiv \sigma_p$ (so that the distribution of $\tilde{x}_j$ is invariant with j) in Eq. (8), one obtains coupled quadratic equations for σ_q^2 and σ_p^2. The resulting σ_q is shown in Fig. 3. The calculated values match the numerical results quite well, and the differences are within the expected deviation for the finite matrix size. The ratio of σ_q and σ_p is

$$\eta \equiv \frac{\sigma_q}{\sigma_p} = \left(\frac{\sum_k \omega_k^{-2} S(\omega_k,\tau)^2}{\sum_k \omega_k^2 S(\omega_k,\tau)^2}\right)^{1/4}. \qquad (9)$$

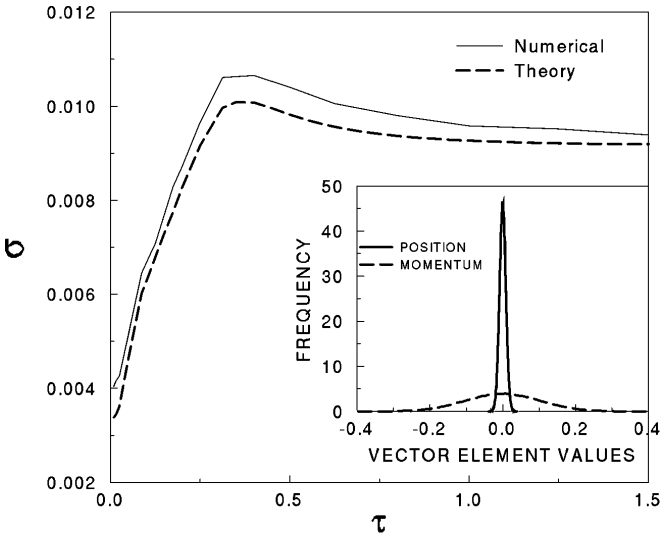

FIG. 3. Variation of σ_q with τ for $T^* = 1.271$. The solid line shows the numerical values. The dashed curve shows the calculated result. The inset shows normalized histograms of values of position and momentum elements for $T^* = 1.271$ and $\tau = 0.225$.

Note that η defines an inverse frequency. The cumulative spectrum obtained with the scaled eigenvalues is shown in Fig. 1 and is seen to be in vastly better agreement with the numerical random matrix spectrum.

It is now possible, within the above framework, to calculate good approximations to the Lyapunov spectra for a liquid, given the INM spectrum and a meaningful estimate of the decorrelation time. I now calculate the maximum Lyapunov exponent, assuming a simple form for the INM spectrum and an *ansatz* for the decorrelation time. The INM spectrum is expressed as

$$\rho(\omega) = \rho_u(\omega) + \rho_s(\omega), \tag{10}$$

where ρ_u (ρ_s) refers to the imaginary (real) frequencies. Both ρ_u and ρ_s are chosen to depend on $|\omega|$ as $|\omega|^2 \exp(-c|\omega|^2)$, and are normalized to $f_u(T)$ and $1 - f_u(T)$, respectively, where $f_u(T)$ is the fraction of imaginary frequencies. The coefficients in the exponent c_u, c_s (for ρ_u and ρ_s) are chosen to make the mean frequencies $|\omega_u|$ and ω_s calculated from the form above equal those obtained in simulation. I use the temperature dependence of $f_u(T)$, $|\omega_u|$, and ω_s as obtained directly from the simulation results and a simple interpolation between simulation data points.

An obvious guess for the decorrelation time τ is that this time scale is set by the mean imaginary frequency in the INM spectrum, since imaginary frequency modes cause exponential "runaway" motion away from the region where the harmonic approximation of the potential around the initial point is valid. Thus, I choose τ to be inversely proportional to the mean imaginary frequency, i.e., $\tau = k/|\omega_u(T)|$; k is a free parameter. With these empirical forms, and with Eq. (7) for the eigenvalues of the $\mathbf{S}'$ matrices, the temperature dependence of $\lambda_{\max}$ is calculated from Eq. (6). The result is shown along with the simulation result in Fig. 2, with the choice $k = 1.79$. The agreement between the calculated and simulation values is excellent except for small deviations at the lowest temperatures, indicating both the validity of the *ansatz* for τ and that the simple form chosen for the INM spectrum is adequate.

Results presented here demonstrate that the Lyapunov spectrum in many body systems can feasibly be calculated in terms of a local description of the potential energy landscape, the INM spectrum. A direct relationship can often be demonstrated for simple low dimensional dynamical systems between Lyapunov exponents and local rates of separation of trajectories. The results presented here show that analogous relations can be obtained for higher dimensional systems as well. While some aspects of the calculations here need further examination, many interesting questions, such as the temperature and density dependence of the shape of the Lyapunov spectra, can be addressed following this approach.

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[1] P. Gaspard and G. Nicolis, Phys. Rev. Lett. **65**, 1693 (1990); J. R. Dorfman and P. Gaspard, Phys. Rev. E **51**, 28 (1995); P. Gaspard and J. R. Dorfman, Phys. Rev. E **52**, 3525 (1995).

[2] E. G. D. Cohen, Physica (Amsterdam) **213A**, 293 (1995); H. A. Posch and W. G. Hoover, Phys. Rev. A **38**, 473 (1988).

[3] R. J. Hinde and R. S. Berry, J. Chem. Phys. **96**, 1376 (1992); R. J. Hinde, R. S. Berry, and D. J. Wales, J. Chem. Phys. **99**, 2942 (1993).

[4] R. S. Berry, Chem. Rev. **93**, 2379 (1993), and references therein; R. S. Berry and R. Breitengraser-Kunz, Phys. Rev. Lett. **74**, 3951 (1995).

[5] T. Keyes, J. Chem. Phys. **101**, 5081 (1994), and references therein.

[6] Y. Wan and R. M. Stratt, J. Chem. Phys. **100**, 5123 (1994), and references therein.

[7] J. E. Straub and D. Thirumalai, Proc. Natl. Acad. Sci. U.S.A. **90**, 809 (1993).

[8] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1989).

[9] See pp. 650, 651 in J.-P. Eckmann and D. Ruelle, Rev. Mod. Phys. **57**, 617, (1985).

[10] G. Benettin, L. Galgani, A. Giorgilli, and J.-M. Strelcyn, Meccanica **15**, 9 (1980).

[11] H. A. Posch and W. G. Hoover, Phys. Rev. A **39**, 2175 (1989).

[12] J.-P. Eckmann and C. E. Wayne, J. Stat. Phys. **50**, 853 (1988).

[13] These vectors are distributed uniformly over the $3N$ unit sphere. Such a distribution (and equivalent distributions whose projection onto the unit sphere have this property) will henceforth be referred to simply as a "uniform distribution."

[14] C. M. Newman, in *Random Matrices and Their Applications*, edited by J. E. Cohen, H. Kesten, and C. M. Newman (AMS, Providence, Rhode Island, 1986), p. 121.

[15] More precisely, vectors $\mathbf{v}_i$ of length M constructed with Gaussian random numbers with zero mean and variance $1/M$ are uniformly distributed (as defined in [13]), with $\mathbf{v}_i \cdot \mathbf{v}_i$ equal to one *plus* deviations distributed with variance $1/M$. The scalar product of two such vectors is zero *plus* deviations distributed with variance $1/M$. The latter two results are easily derived by evaluating the mean and variance of $\mathbf{v}_i \cdot \mathbf{v}_i$ and $\mathbf{v}_i \cdot \mathbf{v}_j$. The first statement follows from noting that the joint distribution for the elements of $\mathbf{v}_i$ is the multivariate normal distribution with a diagonal covariance matrix with identical elements. This distribution is invariant under an orthogonal transformation of variables.