PHYSICAL REVIEW E VOLUME 61, NUMBER 4 APRIL 2000

Structural stability of simple classical fluids: Universal properties of the Lyapunov-exponent measure

G. Malescio,[1,2] P. V. Giaquinta,[1,2] and Y. Rosenfeld[3]

[1]Istituto Nazionale per la Fisica della Materia, Unità di Ricerca di Messina, Contrada Papardo, 98166 Messina, Italy

[2]Dipartimento di Fisica, Università degli Studi di Messina, Contrada Papardo, 98166 Messina, Italy

[3]Physics Department, Nuclear Research Center Negev, P.O. Box 9001, Beer-Sheva 84190, Israel

(Received 22 October 1999)

A threshold for the stability of the solution of integral equations for the pair correlation function of a classical fluid can be determined from the Floquet matrix for the iterative form of the integral equation. Correspondingly, a measure of the structural stability of the fluid, analogous to the Lindemann ratio for a solid, is provided by the Lyapunov exponent λ that is related to the perturbed dynamics. The behavior of λ as a function of density, temperature, interatomic potential, and closure relations for the integral equation, is analyzed and discussed. In analogy with the Lindemann parameter, we find—for the hypernetted-chain-type closures—that $\lambda(T/T_{inst})$ is ''quasiuniversal,'' i.e., very weakly dependent on the interaction potential, up to a temperature $T/T_{inst}\sim 5$, where T_{inst} is the stability-threshold temperature. We show how this result connects the Lyapunov exponent measure of the pair structure with the equation of state of the fluid.

PACS number(s): 05.70.Ce, 05.70.Fh, 61.20.Gy

I. INTRODUCTION

The semiempirical melting criterion proposed by Lindemann in 1910 states that for the three-dimensional (3D) monatomic crystal, on average, the ratio of the root-mean-square (rms) displacement of the atoms from their equilibrium lattice sites $(\langle x^2\rangle)^{1/2}$ to the nearest neighbor distance d is approximately a universal number $\delta=(\langle x^2\rangle)^{1/2}/d=\delta_L\simeq 0.15$ [1,2]. Lindemann's ratio δ is a measure of the structural stability of the solid in the sense that a small value of δ is consistent with the standard picture of a solid, i.e., a system of localized atoms, confined around their equilibrium lattice positions by a ''cage'' made by their neighbors. As the temperature increases or the density decreases, δ increases until it gets so large ($\delta \gtrsim \delta_L$) that localization is destroyed, and the original picture of an ordered solid is no longer *self-consistent*. The ''critical'' value δ_L marks the limit of structural stability of the solid, beyond which another description of the structure is called for. Lindemann's ratio is an example of a measure of the structure which can be used to define a stability limit, because it addresses a feature that is used in the buildup of the structure itself. It is valid for a variety of real and model crystals, quite independently of the specific atomic interactions: Lindemann's limit correlates well with the thermodynamic stability threshold of a solid, namely, with the melting line [1,2].

In two dimensions (2D), the rms displacement of particles in a crystal diverges logarithmically with the system size. However, if written in terms of the Debye temperature, the Lindemann's criterion can be empirically extended also to 2D. Similarly, the Ross generalization [3] of Lindemann's criterion, using the value of the thermal free energy, can be applied (with another threshold value) also in 2D [4]. The defect-mediated Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory of melting in 2D yields a Lindemann-type formula without any adjustable constant [1].

In three dimensions (3D), Hansen and Verlet considered the height of the first peak of the structure factor S_{max} as an analog of Lindemann's criterion on the fluid side, and found that the value $S_{max}\simeq 2.85$ correlates well with the freezing density of simple fluids [5]. The Hansen-Verlet rule, with a larger value for S_{max}, can be used to estimate the freezing line of 2D fluids as well. The ''residual multiparticle entropy'' (RMPE) also provides a measure of the fluid structure which correlates well with the freezing line [6]. This criterion can be successfully applied also in 2D [7,8].

Using the concept of an effective hard-sphere diameter (e.g., in the context of variational thermodynamic perturbation theories), melting and freezing criteria valid for hard-core particles can be extended to fluids with continuous potentials in both 3D and 2D [4,9]. In particular, with the advent of the approximation of universality of the bridge functions [10], a hard-sphere freezing criterion was proposed in terms of the value of the bridge function at zero separation, $b(r=0)$ [4]. It so happens that the freezing rule, $b(r=0)\simeq 50$, applies equally well in both 2D and 3D. A ''dynamical'' criterion for the freezing of colloidal systems, which is valid also in 2D, was proposed by Löwen, Palberg, and Simon [11]. Recently, it was found that hard-core fluids exhibit a structural precursor of the freezing transition, which manifests itself through a shoulder which emerges in the second peak of the radial distribution function [1]. It is not known if such a precursor holds, in general, for monatomic fluids.

Other freezing criteria arise from the properties of solutions of integral equations for the pair distribution function of the fluid [12], or from the instability of the iterative solutions of such equations [13]. In particular, the stability limit of the hypernetted-chain (HNC) equation [14,15] with respect to its defining diagrammatic iteration loop, falls close to the freezing density for a large variety of interaction pair potentials, in both 2D and 3D [13]. Subsequently, a more general analysis revealed that equal results (to within the numerical uncertainty of the calculations) for the threshold density are obtained through a study of the Floquet matrix for the iterative form of the integral equation used for the calculation of the pair structure [16]. More specifically, the Lyapunov exponent related to the dynamics corresponding to the diagrammatic iteration process provides a measure of the pair correlation function of the fluid with a critical (threshold) value signaling the stability limit density ρ_{inst}. Such critical values agree with those obtained by direct observation of the iteration process.

The Lindemann ratio has a rather direct relation to the structure and thermodynamics of the solid, so that the motivation for its definition and the physical meaning of its application are clear. On the other hand, the precise physical meaning of the various measures introduced for the liquid structure, and the reason why their critical values correlate so well with freezing, are not well understood, and deserve further study. Among these, the criterion based on the Lyapunov-exponent measure of the fluid structure seems to be the closest in spirit to Lindemann's measure for the solid, since it addresses the *self-consistency* of a process by which the typical structure (namely, the pair correlation, in the fluid case) is obtained.

In this paper we continue our study of the behavior of the Lyapunov exponent as a function of density, temperature, interaction potential, and closure relations for the integral equation. In Sec. II we recall the definition of the Lyapunov-exponent measure of the structure from our previous work [16]. New results are presented in Sec. III which are analyzed and discussed in Sec. IV. In particular, we find for HNC-type closures that $\lambda(T/T_{inst})$ is nearly ''universal'' when plotted as a function of the ratio T/T_{inst}, where T_{inst} is the stability-threshold temperature. When compared with a recent density-functional-theory (DFT) analysis of the equation of state of simple classical systems [17], this ''universality'' manifestly demonstrates an intimate connection of the Lyapunov-exponent measure of the fluid pair structure with the thermal part of the contribution of the interactions to the equation of state.

II. LYAPUNOV-EXPONENT STABILITY MEASURE

The nonlinear integral equations that are obtained by supplementing the Ornstein-Zernike (OZ) relation with some appropriate closure (viz., an independent relation between the total and direct correlation functions [14]), have the form

$$f(r)=K(r,f(r))+\int K(|\mathbf{r}-\mathbf{s}|,f(|\mathbf{r}-\mathbf{s}|))f(s)d\mathbf{s}, \tag{1}$$

where $f(r)$ typically denotes the total correlation function $h(r)$ and K is a kernel that depends on the approximate closure adopted for $c(r)$. Such integral equations can be written in the form

$$f(r)=Af(r), \tag{2}$$

where $f(r)\in S$ describes the particle distribution of the system investigated, S is a set of a metric space, and $A:S\rightarrow S$ is an operator mapping S onto itself. When applying the simple iterative method to Eq. (2), one generates, starting from some initial value f_0, successive approximations to the solution through the mapping

$$f_{n+1}=Af_n. \tag{3}$$

If the sequence of successive approximations $\{f_n\}$ converges towards a value f^*, then f^* is a fixed point for the operator A, i.e., a solution of Eq. (2): $f^*=Af^*$. The operator A describes how the values assumed by f over the whole system are to be ''processed'' in order to determine the value of f at a given point. As suggested by the fixed-point form of Eq. (2), in a state of thermodynamic equilibrium a condition of ''detailed balance'' holds between the local value of f and that resulting from the resummed contribution of indirect correlations at intermediate points of the system. This sort of internal balance between the local and global properties of the function, which ultimately determines the density profile of the fluid, can be used to define a ''measure'' of the pair structure with a related definition of stability threshold.

In fact [16], let us imagine to perturb the *equilibrium* correlation function $f^*(r)$ by an arbitrary perturbation $\delta(r)$. The perturbed, *nonequilibrium* correlation function $f(r)=f^*(r)+\delta(r)$ is processed by the operator A which, to first order in the perturbation, yields $M\delta(r)$, where the matrix $M=(\partial A/\partial f)|_{f^*}$ is the Floquet matrix acting on the perturbation vector (in numerical applications r is represented by a grid of N points, the function f is an N vector and A is a f-dependent $N\times N$ matrix) [18]. In turn, $M\delta$ can now be considered as a perturbation which, when processed by the system, gives origin to a new perturbation $MM\delta$, and so on. The successive iterations of this procedure generate a *fictitious dynamics* consisting of repeated applications of the Floquet matrix to the initial perturbation δ_0, which can be represented as follows:

$$\frac{\|\delta_n\|}{\|\delta_0\|}=\prod_{i=0}^{n-1} S_i, \tag{4}$$

where

$$S_n=\frac{\|M\delta_n(r)\|}{\|\delta_n(r)\|}, \tag{5}$$

and $\|f(r)\|=\sqrt{(\Sigma_{i=1}^{N})f^2(r_i)}$ is the norm of a function f defined over a mesh of N points. Assuming that the norm of the perturbation depends (as long as it remains infinitesimal) exponentially on the number of iterations, i.e., $\|\delta_n(r)\|=\|\delta_0(r)\|2^{\lambda n}$, where λ is the Lyapunov exponent related to the perturbation dynamics, one can write the average exponential stretching of initially nearby points as

$$\lambda=\lim_{n\to\infty}\frac{1}{n}\log_2\left(\prod_{i=0}^{n-1} S_i\right). \tag{6}$$

The actual number of iterations after which λ reaches its saturation value depends on the density, ranging from a few tens at low density to a few hundreds near the instability point. Though, in principle, the Lyapunov exponent depends on the initial perturbation $\delta_0(r)$, we found [16] that wildly different forms of the initial perturbation lead to essentially

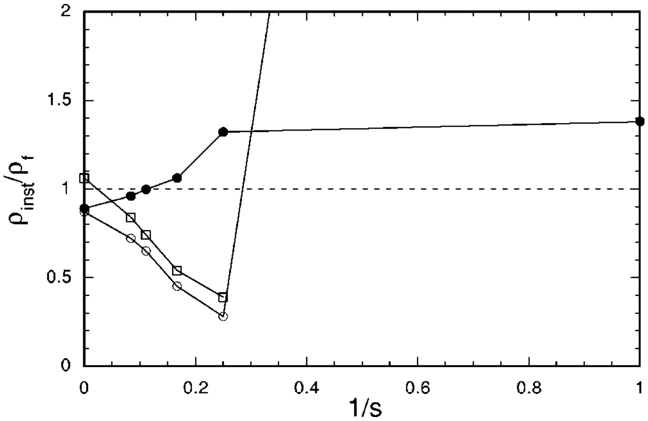

FIG. 1. Ratio of the instability density ρ_{inst} to the freezing density ρ_f for inverse-power potentials, within the HNC (dots), PY (circles), and MS (squares) approximations.

identical values of λ. Consequently, this quantity provides a measure of the stability of the solution, and thus of the stability of the fluid structure as defined through the integral equation.

III. RESULTS

We calculated λ for a variety of pair potentials [hard-sphere, inverse-power, Yukawa, Lennard-Jones (LJ)], and various closures of the OZ integral equation [HNC, Percus-Yevick (PY), Martynov-Sarkisov (MS)] [14,15]. In view of the rather intensive computaions involved we focused attention on the HNC and PY closures, and on the inverse power and Yukawa as two one parameter families of potentials, with only exploratory calculations for the LJ system and the MS closure. For the inverse-power potentials,

$$\phi_s(r)=\epsilon\left(\frac{\sigma}{r}\right)^s, \tag{7}$$

as well as for the LJ potential,

$$\phi_{LJ}(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \tag{8}$$

we use $\rho^*=\rho\sigma^3$ and $T^*=k_BT/\epsilon$ as reduced variables, and, for hard spheres $(s=\infty)$, the packing fraction $\eta=(\pi/6)\rho\sigma^3$. If one measures distances in units of the Wigner-Seitz radius $a_{WS}=(3/4\pi\rho)^{1/3}$, the inverse-power potentials can be written in the form

$$\frac{\phi_s(r)}{k_BT}=\frac{\Gamma}{r^s}, \tag{9}$$

where $\Gamma=(\epsilon/k_BT)(\sigma/a_{WS})^s=[(4\pi/3)\rho^*]^{s/3}/T^*$ is a dimensionless coupling parameter. Correspondingly, the Yukawa potential takes the form

$$\frac{\phi_Y(r)}{k_BT}=\frac{\Gamma}{r}e^{-\alpha r}. \tag{10}$$

The zero-screening case $(\alpha=0)$ obviously reduces to the Coulomb, inverse-power potential $(s=1)$.

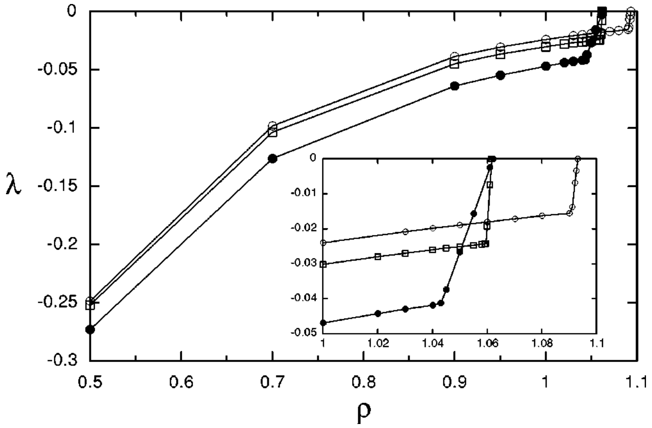

FIG. 2. Lyapunov exponent as function of the reduced density, for the Lennard-Jones potential at $T=2.74$ within the HNC (dots), PY (circles), and MS (squares) approximations.

The ratio of the instability density to the freezing density, ρ_{inst}/ρ_f is plotted in Fig. 1 for the inverse-power potentials as calculated within the PY and HNC equations. The value assumed by ρ_{inst}/ρ_f for the PY approximation in the Coulomb limit is out of scale, being close to 16. We note that, at variance with the PY closure, the value of ρ_{inst} found in the HNC approximation moderately departs from the freezing density in the Coulomb limit only. In this respect, the marked failure of the PY approximation as the potential gets softer and softer looks more dramatic than the loss of accuracy shown by the same approximation in relation to the more standard structural and thermodynamic properties of the model. We conclude that the proposed estimate of the instability threshold reveals as a more stringent test of the physical "soundness" of the closure than its very capacity to account for a reliable representation of the pair structure of the fluid. As can be seen in Fig. 2 for the LJ system at $T^*=2.74$, the various closures' results for ρ^*_{inst} are rather close to $\rho^*_f=1.113$, as expected from their results for the steep inverse power potentials, with the HNC and MS closures behaving similarly.

Figures 3 and 4 show the behavior of the Lyapunov ex-

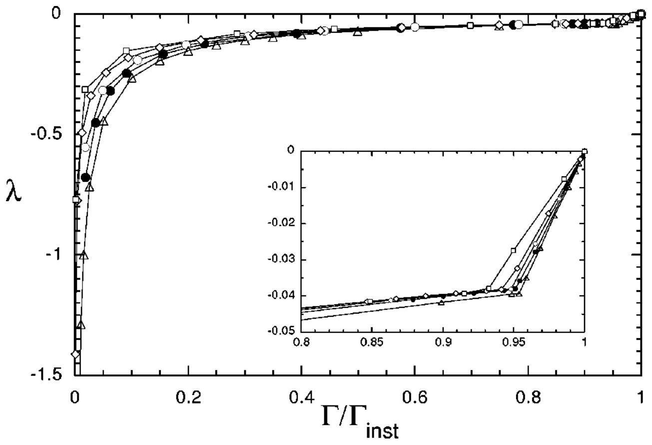

FIG. 3. Lyapunov exponent as function of Γ/Γ_{inst} for inverse power potentials within the HNC approximation. Symbols: triangles $(s=1)$, dots $(s=4)$, circles $(s=6)$, squares $(s=12)$, diamonds (hard-spheres).

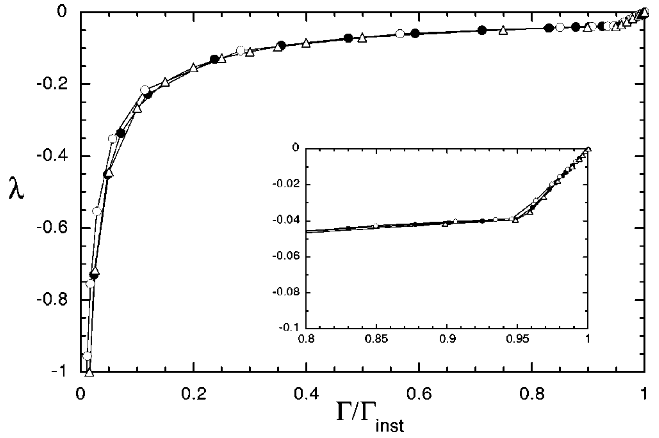

FIG. 4. Lyapunov exponent as function of Γ/Γ_{inst} for Yukawa potentials within the HNC approximation. Symbols: triangles ($\alpha=0$), dots ($\alpha=1.83$), circles ($\alpha=3.34$).

ponent, plotted as a function of the ratio Γ/Γ_{inst}, for the inverse-power and Yukawa potentials, respectively, in the HNC approximation. As the density increases at fixed temperature, λ becomes less and less negative, thus signaling a less efficacious damping of the perturbation (see Sec. II). The slope of the curve, initially rather steep, decreases rapidly but smoothly with the density in such a way that it might appear that the loss of stability of the solution (corresponding to the vanishing of λ), would occur only asymptotically. Instead, at a density ρ_c slightly smaller than ρ_{inst}, the slope of the curve changes abruptly and λ eventually vanishes for $\rho=\rho_{inst}$. As is better seen from the insets of Figs. 3 and 4, two distinct branches meet at ρ_c with a different slope. Indeed, within the limits of numerical accuracy of the calculation, the derivative $d\lambda/d\rho$ has a discontinuity at ρ_c whose value depends on both the potential and the integral closure. However, the general behavior, which was originally observed for hard spheres [16], remains the same.

IV. ANALYSIS AND DISCUSSION

From the results obtained the HNC emerges as the only approximate closure considered here which behaves overall properly for all potentials. The most important result of this work is the finding for the HNC closure (Figs. 3 and 4) that as function of the ratio T/T_{inst}, where T_{inst} is the stability-threshold temperature, the Lyapunov exponent $\lambda(T/T_{inst})$ is quasiuniversal, i.e., very weakly dependent on the interaction potential up to $T/T_{inst}\sim 5$.

In the case of the Lindemann parameter, it is easy to show for a harmonic solid that

$$\delta \propto \left(\frac{T}{K(\rho)}\right)^{1/2}, \tag{11}$$

where $K(\rho)$ is the force constant. Thus, the ratio of δ to its threshold value (at same density) is given by

$$\frac{\delta}{\delta_L}=(T/T_{inst})^{1/2}, \tag{12}$$

which is independent of the pair potential. This reflects the fact that the thermal potential energy (on top of the Madelung, static lattice, energy) for a harmonic solid is given by

$$u_{th}=\frac{3}{2}k_BT=\frac{1}{2}K(\rho)\delta^2 \tag{13}$$

so that the ratio of its value to that at threshold, at constant density, is universal

$$\frac{u_{th}}{u_{th,inst}}=T/T_{inst}. \tag{14}$$

Now, our results for the inverse power potentials and Yukawas show that to good approximation

$$\lambda=f(\Gamma/\Gamma_{inst})=f(T_{inst}/T) \tag{15}$$

is a universal function of T/T_{inst}, independent of potential, for both the HNC approximate closure and other related closures, with slightly different values for the function *f*. It can be shown from the equation of state for these fluids that [19,18] if we subtract from the potential energy a *fluid* Madelung term in order to obtain a thermal potential energy u_{th}, we obtain a nearly universal dependence of the ratio T_{inst}/T,

$$\frac{u_{th}}{u_{th,inst}}=g(\Gamma/\Gamma_{inst})=g(T_{inst}/T), \tag{16}$$

for both the HNC approximation and numerical simulation results, with slightly different functions *g*. Specifically [18,19]

$$g(0.1\lesssim x\lesssim 1)\simeq x^{1/2}\ \ \text{(HNC)},$$

$$g(0.1\lesssim x\lesssim 1)\simeq x^{2/5}\ \ \text{(simulation)}. \tag{17}$$

Thus, similarly to the Lindemann ratio, the Lyapunov-exponent measure exhibits a nearly universal behavior, when expressed as function of the ratio of the temperature to the threshold temeperature, and this scaling property is shared with the thermal potential energy. On the basis of the fundamental-measure free energy functional for hard spheres and thermodynamic perturbation theory, a unified analytic description of classical bulk solids and fluids was obtained recently [18], predicting correctly major features of their equations of state and freezing parameters as obtained by simulations. The fundamentally different fluid and solid asymptotic high density expansions for the potential energy, featuring a static-lattice Madelung term and the harmonic $\frac{3}{2}k_BT$ correction, on one hand, and a fluid Madelung energy with a $\sim T^{3/5}$ thermal energy correction, on the other, *both originate from the same singularity* in the *hard-sphere* free energy functional. A similar asymptotic behavior, with the same fluid Madelung energy but with a different exponent for the thermal energy, is exhibited by the HNC approximation [19]. It appears from these studies [19,18] that the fluid structure for repulsive potentials can be represented by an asymptotic high-density expansion, and the scaling relations in terms of Γ/Γ_{inst} are manifestations of this property. From this point of view, the Lyapunov-exponent measure, even though not directly measuring a fluid structure parameter (like the height of the first peak of the structure factor) can nevertheless be related to the asymptotic expansion.

[1] T.M. Truskett, S. Torquato, S. Sastry, P.G. Debenedetti, and F. Stillinger, Phys. Rev. E **58**, 3083 (1998).

[2] H. Löwen, Phys. Rep. **237**, 249 (1994).

[3] M. Ross, Phys. Rev. **184**, 233 (1969).

[4] Y. Rosenfeld, Phys. Rev. A **24**, 2805 (1981).

[5] J.P. Hansen and L. Verlet, Phys. Rev. **184**, 151 (1969).

[6] P.V. Giaquinta and G. Giunta, Physica A **187**, 145 (1992); P.V. Giaquinta, G. Giunta, and S. Prestipino Giarritta, Phys. Rev. A **45**, 6966 (1992).

[7] M.G. Donato, S. Prestipino, and P.V. Giaquinta, Eur. Phys. J. B (to be published).

[8] S. Prestipino, F. Saija, and P.V. Giaquinta (unpublished).

[9] Y. Rosenfeld and R. Thieberger, Phys. Rev. A **15**, 1269 (1977), and references therein; Y. Rosenfeld, J. Phys. C **15**, L437 (1982).

[10] Y. Rosenfeld and N.W. Ashcroft, Phys. Rev. A **20**, 1208 (1979).

[11] H. Löwen, T. Palberg, and R. Simon, Phys. Rev. Lett. **70**, 1557 (1993).

[12] J. Kozac, *Nonlinear Problems in the Theory of Phase Transitions*, edited by I. Prigogine and S.A. Rice, Advances in Chemical Physics Vol. XL (Wiley, New York, 1979).

[13] Y. Rosenfeld, Phys. Rev. A **43**, 6526 (1991); **46**, 4922 (1992).

[14] J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic Press, London, 1986).

[15] R. Evans, in *Liquids at Interfaces*, edited by J. Chavrolin, J.F. Joanny, and J. Zinn-Justin (Elsevier, Amsterdam, 1989).

[16] G. Malescio, P.V. Giaquinta, and Y. Rosenfeld, Phys. Rev. E **57**, R3723 (1998).

[17] Y. Rosenfeld and P. Tarazona, Mol. Phys. **95**, 141 (1998).

[18] See, for example, P. Bergé, Y. Pomeau, and C. Vidal, *Order within Chaos* (Wiley, Paris, 1986).

[19] Y. Rosenfeld, Phys. Rev. A **32**, 1834 (1985); **33**, 2025 (1986).