Morphological ordering in biopolymers: Informational statistical thermodynamic approach

Sergio A. Hassan,[1] Marcus V. Mesquita,[2] Aurea R. Vasconcellos,[2] and Roberto Luzzi[2]

[1]*Department of Physiology and Biophysics, Mount Sinai School of Medicine, New York, New York 10029-6574*

[2]*Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas,*
Unicamp, 13083-970 Campinas, São Paulo, Brazil

We consider the question of the emergence of morphological ordering in an open far-from-equilibrium model of a biopolymer. We apply informational statistical thermodynamics, which was shown to be appropriate to deal with dissipative systems displaying complex behavior. The formation of nonlinear spatial ordering consisting in the emergence of static charge-density waves, producing a bioelectret-type state, is evidenced. This kind of behavior may arise in biopolymers under the influence of biochemical processes.

I. INTRODUCTION

In the field of systems with complex behavior (*complex systems* for short) [1–3], the study of self-organization with emergence of *dissipative structures* has deserved special interest [4–7]. We address here the possibility of the emergence of morphological ordering in quasilinear systems, e.g., biopolymers, when driven far from equilibrium. It is shown that the interplay of collective behavior (plasma waves) coupled to dissipative processes can lead to the emergence of such spatial ordering.

We deal with this question on the basis of the so-called *thermodynamics of complexity* [8], which is the application of informational-statistical thermodynamics (IST) [9–13] to the study of complex systems. The present development of IST is based on a nonequilibrium ensemble formalism, which is a far-reaching generalization of Gibbs and Boltzmann approaches, labeled the nonequilibrium statistical operator method [14–17]. Its formulation is based on a variational principle, namely, the principle of maximization of the informational entropy [18], and then referred to as MaxEnt-NESOM for short.

A by-product of MaxEnt-NESOM is a generalized nonlinear quantum kinetic theory [14,19,20]. It provides the equations of evolution for the basic variables describing the irreversible change in time of the macroscopic state of the nonequilibrium system. The connection with complexity is given by the nonlinear terms that are known to be necessary for complex behavior to arise.

Recent theoretical studies have suggested the possibility of the emergence of a morphological transition in carrier systems in bulk matter when under the action of an external source of energy [21]. Later work [22] has confirmed this result in the case of polar semiconductors continuously illuminated with ultraviolet radiation. It was shown that the ordered states consist of the formation of stationary charge-density waves. However, it was pointed out that the observation of this phenomenon under accessible experimental conditions could be unfeasible because of the intense illumination required. In effect, because of the poor efficiency of the absorption of light, high pumping intensities are necessary to overcome dissipative effects and provide for pattern formation, which could produce damage in the sample.

In the same paper [22] the possibility was conjectured that the situation may improve in the case of systems with low dimensionality (like semiconductor quantum wires). In particular, it is expected that such phenomenon may follow more easily in the case of biopolymers, e.g., the α-helix secondary structure in protein and peptides, DNA chains, etc. [23], as well as in doped organic polymers, like vinyls, acetanilide, etc. [24,25]. We note that biopolymers behave as semiconductorlike materials of the p-doped type [26], and admit efficient mechanisms of excitation via biochemical processes (see, for example, [27]). This is an interesting point as it was proposed that mobile electrons can have an important effect in biological systems [28].

We consider here a problem of this kind, namely, electronic carriers in quasi-one-dimensional p-type conducting materials, in particular a wirelike biopolymer. We show how morphological patterns in the carrier system can emerge as long-lived spatially organized charges, that is, a kind of bioelectret state [29]. We present a characterization of the instability and an analysis of the spatial organization of the carrier system.

II. INSTABILITY OF THE HOMOGENEOUS STATE

We consider a quasi-one-dimensional system of a p-doped type, consisting of a periodic lattice with lattice parameter a. Let n_h be the density of holes (carriers in the valence or bonding band), and n_e the density of electrons (carriers in the conduction or antibonding band). The density n_e is a result of thermal excitation or other processes of excitation, and let n_h be much larger than n_e. Moreover, the concentration n_h is considered to be high enough for the carrier system to be on the metallic side of Mott transition [30] (this is the case in proteins, where the density is of the order of 10^{18} cm^{-3} [26]), i.e., impurity states and excitons are totally ionized with holes and electrons acting as mobile carriers. Furthermore, these carriers are driven away from equilibrium by an external pumping source (e.g., electromagnetic radiation or biochemical excitation [27] in the case of biosystems).

The system Hamiltonian is taken as

$$\hat{H} = \hat{H}_0 + \hat{H}' + \hat{H}_f, \tag{1}$$

where

$$\hat{H}_0 = \hat{H}_c + \hat{H}_L, \tag{2}$$

with

$$\hat{H}_c = \sum_{\mathbf{k}} [\epsilon_{\mathbf{k}}^h h_{-\mathbf{k}}^\dagger h_{-\mathbf{k}} + \epsilon_{\mathbf{k}}^e c_{\mathbf{k}}^\dagger c_{\mathbf{k}}], \tag{3}$$

which is the Hamiltonian of the mobile carriers, with $c_k(c_k^\dagger)$ and $h_k(h_k^\dagger)$ being annihilation (creation) operators of electrons and holes in states $\mathbf{k}$ (in antibonding or bonding bands, respectively), $\epsilon_{\mathbf{k}}^e$ and $\epsilon_{\mathbf{k}}^h$ are the corresponding energy dispersion relations, and

$$\hat{H}_L = \sum_{\mathbf{q}\gamma} \hbar \omega_{\gamma\mathbf{q}} \left(b_{\gamma\mathbf{q}}^\dagger b_{\gamma\mathbf{q}} + \frac{1}{2} \right) \tag{4}$$

is the Hamiltonian associated with the lattice vibrations, with $b(b^\dagger)$ being annihilation (creation) operators of phonons in mode $\mathbf{q}$ of branch γ; $\mathbf{k}$ and $\mathbf{q}$ run over the Brillouin zone. The interaction Hamiltonian between carriers and lattice is given by

$$\hat{H}' = \sum_{\mathbf{k}\mathbf{q}\gamma l} [V_{\gamma\mathbf{q}}^{l(h)} h_{-\mathbf{k}+\mathbf{q}}^\dagger h_{-\mathbf{k}} + V_{\gamma\mathbf{q}}^{l(e)} c_{\mathbf{k}+\mathbf{q}}^\dagger c_{\mathbf{k}}](b_{\gamma\mathbf{q}} - b_{\gamma-\mathbf{q}}^\dagger), \tag{5}$$

where $V_{\gamma\mathbf{q}}^l$ are the matrix elements of the interaction and l indicates the type of interaction: deformation potential in all cases, plus Fröhlich interaction with longitudinal optical vibrations, and piezoelectric potential with acoustic vibration [31]. Finally, the Hamiltonian of the interaction of the carriers with the external source is given by

$$\hat{H}_f = \sum_{\mathbf{k}\kappa} [\lambda_\kappa^{(h)} \varphi_\kappa h_{-\mathbf{k}+\kappa}^\dagger h_{-\mathbf{k}} + \lambda_\kappa^{(e)} \varphi_\kappa c_{\mathbf{k}+\kappa}^\dagger c_{\mathbf{k}}] + \text{H.c.}, \tag{6}$$

where the φ are annihilation operators of elementary excitations in the source (which "feeds" the system with energy and momentum), λ is the coupling strength, and κ is the quasimomentum—or crystalline momentum—transferred in the process. We keep the vector notation for $\mathbf{k}$, $\mathbf{q}$, etc., since both directions of propagation along the length of the system are possible.

According to MaxEnt-NESOM we next need to specify the basic set of variables for the description of the nonequilibrium macroscopic state of the system characterized by the Hamiltonian of Eq. (1). This is done in terms of the energy $E_c(t)$, the concentrations n_e and n_h (these densities are constant once they are fixed by doping and thermal excitation [32,33]) [34,35], and the quantities

$$n_{\mathbf{kQ}}^e(\mathbf{t}) = \text{Tr}\{\hat{n}_{\mathbf{kQ}}^e \varrho(t)\}, \qquad n_{\mathbf{kQ}}^h(t) = \text{Tr}\{\hat{n}_{\mathbf{kQ}}^h \varrho(t)\}, \tag{7}$$

where

$$\hat{n}_{\mathbf{kQ}}^e(t) = c_{\mathbf{k}+1/2\mathbf{Q}}^\dagger c_{\mathbf{k}-1/2\mathbf{Q}}, \qquad \hat{n}_{\mathbf{kQ}}^h(t) = h_{-\mathbf{k}-1/2\mathbf{Q}} h_{-\mathbf{k}+1/2\mathbf{Q}}^\dagger. \tag{8}$$

In Eqs. (7), $\varrho(t)$ is the corresponding MaxEnt-NESOM nonequilibrium statistical operator, which is expressed in terms of the basic set of dynamical variables [14–17].

Concerning the lattice subsystem, we would need to introduce the populations of the phonons in the different branches and modes. However, since we are interested in the steady state and not in ultrafast transients, we can take the phonon modes as thermalized with an external reservoir at temperature T_0, and, then, the lattice has a constant energy E_L. Therefore, the phonons are described by a canonical distribution with populations given by the Planck-like form

$$\nu_{\gamma\mathbf{q}} = [\exp\{\hbar\omega_{\gamma\mathbf{q}}/k_B T_0\} - 1]^{-1}. \tag{9}$$

We stress here that the quantities of Eqs. (7) are necessary to describe the spatial ordering in the carrier system. Thus the basic set of macrovariables is

$$\{E_c(t), n_e, n_h, \{n_{\mathbf{kQ}}^e(t)\}, \{n_{\mathbf{kQ}}^h(t)\}, E_L\}, \tag{10}$$

which defines the nonequilibrium thermodynamic space of states (or Gibbs space) of the system.

The MaxEnt-NESOM statistical operator is given, in the Zubarev approach [14], by

$$\varrho_\varepsilon(t) = \exp\left\{ -\hat{S}(t,0) + \int_{-\infty}^t dt' \, e^{\varepsilon(t-t')} \right.$$
$$\left. \times \frac{d}{dt'} \hat{S}(t', t'-t) \right\}, \tag{11}$$

where, in the present case,

$$\hat{S}(t,0) = \phi(t) + \beta_c(t)[\hat{H}_c - \mu_e \hat{N}_e - \mu_h(t) \hat{N}_h]$$
$$+ \beta_0 \hat{H}_L + \sum_{\mathbf{kQ}} [F_{\mathbf{kQ}}^e(t) \hat{n}_{\mathbf{kQ}}^e + F_{\mathbf{kQ}}^h(t) \hat{n}_{\mathbf{kQ}}^h], \tag{12}$$

which is the so-called informational-statistical entropy operator [36,37], and

$$\hat{S}(t', t'-t) = \exp\left\{ -\frac{1}{i\hbar}(t'-t)\hat{H} \right\} \hat{S}(t',0)$$
$$\times \exp\left\{ \frac{1}{i\hbar}(t'-t)\hat{H} \right\}. \tag{13}$$

The function $\phi(t)$ in Eq. (12) ensures the normalization of the statistical operator [it plays the role of the logarithm of a nonequilibrium partition function, $\phi(t) = \ln \bar{Z}(t)$]. In Eq. (11), ϵ is a positive infinitesimal which goes to zero after the calculation of averages have been performed (the exponential with ϵ ensures the irreversible evolution of the system from the initial state) [14–17,38]. Equation (12) contains the corresponding basic set of Lagrange multipliers—associated with the basic set of macrovariables given in Eq. (10)—that the variational method introduces, namely,

$$\{\beta_c(t), \mu_e(t), \mu_h(t), \{F_{\mathbf{kQ}}^c(t)\}, \{F_{\mathbf{kQ}}^h(t)\}, \beta_0\}, \tag{14}$$

which constitutes a set of intensive nonequilibrium thermodynamic variables. The macroscopic state of the system is completely described by the set defined in Eq. (14), or, equivalently, by the set of macrovariables of Eq. (10) [10–17,38].

We introduce the alternative form $\beta_c(t) \equiv 1/k_B T_c^*(t)$ where T_c^* is called the quasitemperature of the thermalized nonequilibrium carriers, and μ_e and μ_h are quasi-chemical potentials [34,35,39,40]. For the particular case of the phonons in equilibrium with the reservoir we have $\beta_0 = 1/k_B T_0$. The functions F in Eq. (14) are the Lagrange multipliers associated with the inhomogeneities in the carrier system. Once the steady state is achieved all these quantities become time independent.

Let us now consider the equations of evolution for the basic macrovariables of Eq. (10), which are consistently derived in the MaxEnt-NESOM-based nonlinear quantum kinetic theory [20]. Formally, these are Heisenberg equations of motion for the basic dynamical variables averaged over the nonequilibrium ensemble, which can be written in terms of collision operators [20]. We restrict the calculations to the Markovian limit [41], that is a satisfactory approach in this case of weak coupling [42]. This can be considered as a far-reaching generalization of Mori-Heisenberg-Langevin equations [43], and we recall that the Markovian approximation implies in retaining binary collisions only.

The equation of evolution for the carriers' energy is

$$\frac{d}{dt}E_c(t) = J_{cf}^{(2)}(t) + J_{cL}^{(2)}, \tag{15}$$

where

$$J_{cf}^{(2)}(t) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}a\kappa} I_\kappa [(\omega)|\lambda_\mathbf{k}|^2 \epsilon_\mathbf{k}^a (f_{\mathbf{k}+1/2\kappa}^a(t)$$
$$-f_{\mathbf{k}-1/2\kappa}^a(t))]\delta(\hbar\omega - \epsilon_{\mathbf{k}+1/2\kappa}^a + \epsilon_{\mathbf{k}+1/2\kappa}^a) \tag{16}$$

corresponds to the rate of energy pumped by the external source, and where we have used a spectral representation in the form

$$\langle \varphi_\kappa^\dagger \varphi_\kappa(t) \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} I_\kappa(\omega) e^{i\omega t}. \tag{17}$$

Moreover,

$$J_{cL}^{(2)}(t) = -\frac{2\pi}{\hbar} \sum_{\mathbf{kq}\gamma l} \sum_a |V_{\gamma\mathbf{q}}^{l(a)}|^2 (\epsilon_{\mathbf{k}+1/2\mathbf{q}}^a - \epsilon_{\mathbf{k}-1/2\mathbf{q}}^a)$$
$$\times \{\nu_{\gamma\mathbf{q}} f_{\mathbf{k}-1/2\mathbf{q}}^a(t)[1 - f_{\mathbf{k}+1/2\mathbf{q}}^a(t)] - [1 + \nu_{\gamma\mathbf{q}}]$$
$$\times [1 - f_{\mathbf{k}-1/2\mathbf{q}}^a(t)] f_{\mathbf{k}+1/2\mathbf{q}}^a(t)\}$$
$$\times \delta(\epsilon_{\mathbf{k}+1/2\mathbf{q}}^a - \epsilon_{\mathbf{k}-1/2\mathbf{q}}^a - \hbar\omega_{\gamma\mathbf{q}}) \tag{18}$$

is the rate of energy exchange between the carriers and the lattice, where $a = e$ or h for electron or hole, respectively. We recall that γ stands for the index of the different branches of phonons and l for the different types of carrier-phonon inter-

actions; the populations $\nu_{\gamma\mathbf{q}}$ are given by Eq. (9); $f_\mathbf{k}^{e(h)}(t)$ are the populations of carriers at time t and V are the matrix elements of the carrier-phonon interactions [cf. Eq. (5)].

Finally, the evolution equations of the variables describing the inhomogeneities of the system, derived in the random-phase approximation (cf., for example [33,44]), are given by

$$\frac{d}{dt}\mathbf{n}_Q^e(t) = \mathbf{\Phi}^e(\mathbf{Q},t), \tag{19}$$

$$\frac{d}{dt}\mathbf{n}_Q^h(t) = \mathbf{\Phi}^h(\mathbf{Q},t), \tag{20}$$

where $\mathbf{n}_Q^{e(h)}$ stands for a column vector with components $n_{\mathbf{kQ}}^{e(h)}(t)$ with fixed $\mathbf{Q}$, and $\mathbf{\Phi}^{e(h)}$ stands for column vectors with components

$$\Phi_{\mathbf{kQ}}^e = -\frac{1}{i\hbar} E_{\mathbf{kQ}}^e n_{\mathbf{kQ}}^e + \frac{1}{i\hbar} \mathcal{V}(\mathbf{Q}) \Delta f_{\mathbf{kQ}}^e n(\mathbf{Q},t)$$
$$- A_{\mathbf{kQ}}^e(t) n_{\mathbf{kQ}}^e(\mathbf{t}) + A_{\mathbf{kQ}}^h(t) n_{\mathbf{kQ}}^h(\mathbf{t}) + \mathcal{R}_{\mathbf{kQ}}^e(\mathbf{t}) + N_{\mathbf{kQ}}^e(\mathbf{t}), \tag{21a}$$

$$\Phi_{\mathbf{kQ}}^h = -\frac{1}{i\hbar} E_{\mathbf{kQ}}^h n_{\mathbf{kQ}}^h - \frac{1}{i\hbar} \mathcal{V}(\mathbf{Q}) \Delta f_{\mathbf{kQ}}^h n(\mathbf{Q},\mathbf{t})$$
$$- A_{\mathbf{kQ}}^h(t) n_{\mathbf{kQ}}^h(t) + A_{\mathbf{kQ}}^e(t) n_{\mathbf{kQ}}^e(t) + \mathcal{R}_{\mathbf{kQ}}^h(\mathbf{t}) + N_{\mathbf{kQ}}^h(t), \tag{21b}$$

where $\mathcal{V}(\mathbf{Q})$ is the matrix element of the Coulomb interaction between carriers, and we have introduced the quantities

$$E_{\mathbf{kQ}}^{e(h)} = \epsilon_{\mathbf{k}+1/2\mathbf{Q}}^{e(h)} - \epsilon_{\mathbf{k}-1/2\mathbf{Q}}^{e(h)}, \tag{22a}$$

$$\Delta f_{\mathbf{kQ}}^{e(h)} = f_{\mathbf{k}+1/2\mathbf{Q}}^{e(h)} - f_{\mathbf{k}-1/2\mathbf{Q}}^{e(h)}. \tag{22b}$$

In the quasi-one-dimensional system (say, a wirelike cylinder with radius R) the matrix element of Coulomb interaction in Eqs. (21) is given by $\mathcal{V}(\mathbf{Q}) = (2e^2/\varepsilon_0 L) K_0(QR)$, with K_0 being the Bessel function of order zero. The contributions $\mathcal{R}_{kQ}^a$ correspond to the carrier-phonon interaction, and $\mathcal{N}_{\mathbf{kQ}}^a(t)$ are bilinear contributions in $n_{\mathbf{kq}}^a$, with $a = e$ or h; for simplicity we omit writing down the cumbersome expressions for these two contributions, since they are not going to be used explicitly in what follows. Finally,

$$A_{\mathbf{kQ}}^a(t) = |\lambda_\mathbf{Q}^{(a)}|^2 I_\mathbf{Q}(E_{\mathbf{kQ}}^a/\hbar) \tag{23}$$

is the contribution arising out of the coupling with the external source, $\lambda_\mathbf{Q}^{(a)}$ is introduced in Eq. (6), and $I_\mathbf{Q}$ is defined in Eq. (17).

In the absence of the source ($I_\mathbf{Q} = 0$), Eqs. (19) and (20) describe the different kinds of mechanical motions [33] averaged over the *equilibrium* state when the nonlinear terms can be neglected (i.e., taking $\mathcal{N}_{\mathbf{kQ}}^a = 0$, since the amplitudes

are very small). They correspond to the single-particle excitations with the excitation spectrum given by the Bohr frequencies

$$\omega_{\mathbf{kQ}}^a = (\epsilon_{\mathbf{k}+1/2\mathbf{Q}}^a - \epsilon_{\mathbf{k}-1/2\mathbf{Q}}^a)/\hbar = E_{\mathbf{kQ}}^a/\hbar, \tag{24}$$

and two types—for this double component plasma—of collective excitations consisting in the so-called *upper* and *lower* plasma waves (plasmons), with, respectively, the dispersion relations

$$\omega_+(\mathbf{Q}) = \xi_+ Q \sqrt{|\ln(QR)|}, \tag{25}$$

$$\omega_-(\mathbf{Q}) = \xi_- Q, \tag{26}$$

for the quasi-one-dimensional system (in the case of bulk samples they correspond to the so-called optical and acoustical branches of plasma wave excitations). In Eqs. (25) and (26) $\xi_\pm$ are constants with dimension of velocity. The expressions of Eqs. (24)–(26) correspond to the frequencies of possible oscillation in the system, but the motion is of course dampened because of the interaction with the lattice vibrations, an effect carried on by the terms $\mathcal{R}$ in the equations of evolution. We recall that the collective excitations are a result of the presence of Coulomb interaction in the term containing $\mathcal{V}(Q)$.

Let us consider the steady state that sets in—after a rapid transient has elapsed—when the system is kept under the constant action of the external source. The homogeneous steady state is characterized by the constant-in-time variables E_c, n_e, n_h, and E_L. In the steady state we have that $dE_c/dt = 0$ in Eq. (15), meaning a balance between the rate of pumped energy [Eq. (16)] and the rate of energy relaxed to the phonons [Eq. (18)]. Except at very high levels of excitation, the phonons can maintain the global carrier's energy in equilibrium at a quasitemperature $T_c^* \approx T_0$.

We proceed next to analyze the behavior of variables $n_{\mathbf{kQ}}^a$ ($a = e$ or h), that are null in the homogeneous steady state, looking for the possible instability of this stationary state against the formation of a spatial pattern, i.e., when $n_{\mathbf{kQ}}^a$ can become different from zero in steady conditions. For that purpose we use standard linear stability analysis, and we test the evolution of $n_{\mathbf{kQ}}^a$ after imposing an arbitrary small perturbation of the form

$$n_{\mathbf{kQ}}^a = \eta_{\mathbf{kQ}}^a e^{\lambda t}, \tag{27}$$

where η is an arbitrary infinitesimal amplitude and λ is the complex number $\lambda = i\omega - \gamma$, where γ and ω are real numbers. Since the amplitudes for the inhomogeneities are null in the homogeneous state, the quantities $\mathcal{N}_{\mathbf{kQ}}^a(t)$ in Eqs. (21) can be neglected since they are bilinear in the amplitudes η.

At low intensities of the pumping source the quantity γ is positive, the perturbation of Eq. (27) only regresses, and the homogeneous stationary state remains stable. This is the so-called thermally chaotic regime corresponding to the linear regime around equilibrium where Prigogine's theorem of minimum entropy production [6] excludes the possibility of emergence of complex behavior. If an instability arises at a sufficient high intensity of the pumping source, i.e., when a

"sufficient distance" from the Onsagerian regime has been achieved, it is characterized by $\gamma = 0$ at this critical intensity. Then, taking $\gamma = 0$ in Eq. (27) and introducing the resulting expression in the linear part of Eqs. (21), we find for each component $n_{\mathbf{kQ}}^a(t)$ that

$$\hbar\omega\eta_{\mathbf{kQ}}^e \equiv \hbar\omega_{\mathbf{kQ}}^e \eta_{\mathbf{kQ}}^e - \mathcal{V}(\mathbf{Q})[\bar{f}_{\mathbf{k}+1/2\mathbf{Q}}^e - \bar{f}_{\mathbf{k}-1/2\mathbf{Q}}^e]\bar{n}(\mathbf{Q})$$
$$+ i\hbar A_{\mathbf{Q}}^e \eta_{\mathbf{kQ}}^e - i\hbar A_{\mathbf{Q}}^h \eta_{\mathbf{kQ}}^h, \tag{28a}$$

$$\hbar\omega\eta_{\mathbf{kQ}}^h \equiv -\hbar\omega_{\mathbf{kQ}}^h \eta_{\mathbf{kQ}}^h + \mathcal{V}(\mathbf{Q})[\bar{f}_{\mathbf{k}+1/2\mathbf{Q}}^h - \bar{f}_{\mathbf{k}-1/2\mathbf{Q}}^h]\bar{n}(\mathbf{Q})$$
$$+ i\hbar A_{\mathbf{Q}}^h \eta_{\mathbf{kQ}}^h - i\hbar A_{\mathbf{Q}}^e \eta_{\mathbf{kQ}}^e, \tag{28b}$$

where the electron-phonon contributions, $\mathcal{R}^a$ in Eqs. (21), have been neglected. In Eqs. (28) we have introduced the function

$$\bar{f}_k^a = [1 + \exp\{\beta[\epsilon_k^a - \mu_a]\}]^{-1}, \tag{29}$$

with $\beta \simeq 1/k_B T_0$, μ_a being the chemical potentials at temperature T_0 and densities n_e and n_h, and

$$\bar{n}(\mathbf{Q}) = \sum_{\mathbf{k}} (\eta_{\mathbf{kQ}}^e + \eta_{\mathbf{kQ}}^h). \tag{30}$$

We notice that in the usual conditions, i.e., $T_0 \simeq 300$ K and n_h of the order or smaller than 10^6 cm^{-1}, the populations in the homogeneous steady state of Eq. (29) can be approximated by

$$\bar{f}_{\mathbf{k}}^a \simeq \left(\frac{2\pi\hbar^2}{m_a^* k_B T_0}\right)^{1/2} n_a \exp\{-\epsilon_k^a/k_B T_0\}, \tag{31}$$

an expression resembling a Maxwell-Boltzmann distribution at temperature T_0 and concentrations n_e and n_h for a quasi-one-dimensional system.

Having fixed $\gamma = 0$ we now look for the eigenvalues $\lambda = i\omega$, which are the roots of the characteristic equations obtained after we add both Eqs. (28) and next sum over $\mathbf{k}$, i.e.,

$$\bar{n}(\mathbf{Q})\varepsilon(\mathbf{Q},\omega) = 0, \tag{32}$$

where

$$\varepsilon(\mathbf{Q},\omega) = 1 - \mathcal{V}(\mathbf{Q})\sum_{\mathbf{k}} \frac{j_1(\mathbf{k},\mathbf{Q},\omega) + ij_2(\mathbf{k},\mathbf{Q},\omega)}{j_B(\mathbf{k},\mathbf{Q},\omega) + ij_4(\mathbf{k},\mathbf{Q},\omega)}, \tag{33}$$

with

$$j_1(\mathbf{k},\mathbf{Q},\omega) = -\Delta f_{\mathbf{kQ}}^e(\hbar\omega - E_{\mathbf{kQ}}^h)$$
$$+ \Delta f_{\mathbf{kQ}}^h(\hbar\omega - E_{\mathbf{kQ}}^e), \tag{34a}$$

$$j_2(\mathbf{k},\mathbf{Q},\omega) = (\Delta f_{\mathbf{kQ}}^e - \Delta f_{\mathbf{kQ}}^h)(A_{\mathbf{kQ}}^e + A_{\mathbf{kQ}}^h), \tag{34b}$$

$$j_3(\mathbf{k},\mathbf{Q},\omega) = (\hbar\omega - E_{\mathbf{kQ}}^e)(\hbar\omega + E_{\mathbf{kQ}}^h), \tag{34c}$$

$$j_4(\mathbf{k},\mathbf{Q},\omega) = -(\hbar\omega + E_{\mathbf{kQ}}^h)A_{\mathbf{kQ}}^h$$
$$-(h\omega - E_{\mathbf{kQ}}^e)A_{\mathbf{kQ}}^e. \tag{34d}$$

Equation (32) has two solutions; one is $\bar{n}(\mathbf{Q})=0$ which corresponds to the homogeneous state (with $n_{\mathbf{kQ}}=0$) and a second one, for $\bar{n}(\mathbf{Q})\neq 0$, that corresponds to the emergence of a spatiotemporal ordering, i.e.,

$$\varepsilon(\mathbf{Q},\omega)=\varepsilon'(\mathbf{Q},\omega)+i\varepsilon''(\mathbf{Q},\omega)=0, \qquad (35)$$

which requires that both the real (ε') and imaginary (ε'') parts are zero, i.e.,

$$\varepsilon'(\mathbf{Q},\omega)=1-\mathcal{V}(\mathbf{Q})\sum_{\mathbf{k}}\frac{\mathcal{M}'(\mathbf{k},\mathbf{Q},\omega)}{\mathcal{D}(\mathbf{k},\mathbf{Q},\omega)}=0, \qquad (36a)$$

$$\varepsilon''(\mathbf{Q},\omega)=-\mathcal{V}(\mathbf{Q})\sum_{\mathbf{k}}\frac{\mathcal{M}''(\mathbf{k},\mathbf{Q},\omega)}{\mathcal{D}(\mathbf{k},\mathbf{Q},\omega)}=0, \qquad (36b)$$

with

$$\mathcal{M}'(\mathbf{k},\mathbf{Q},\omega)=j_1(\mathbf{k},\mathbf{Q},\omega)j_3(\mathbf{k},\mathbf{Q},\omega)$$
$$+j_2(\mathbf{k},\mathbf{Q},\omega)j_4(\mathbf{k},\mathbf{Q},\omega), \qquad (37a)$$

$$\mathcal{M}''(\mathbf{k},\mathbf{Q},\omega)=j_2(\mathbf{k},\mathbf{Q},\omega)j_3(\mathbf{k},\mathbf{Q},\omega)$$
$$-j_1(\mathbf{k},\mathbf{Q},\omega)j_4(\mathbf{k},\mathbf{Q},\omega), \qquad (37b)$$

$$\mathcal{D}(\mathbf{k},\mathbf{Q},\omega)=[j_3(\mathbf{k},\mathbf{Q},\omega)]^2+[j_4(\mathbf{k},\mathbf{Q},\omega)]^2. \qquad (37c)$$

An analysis of Eqs. (36) shows that ε' is an even function of ω while ε'' is an odd function, and it can be shown that there is *not* a simultaneous solution of the system for a *frequency ω different from zero* (moreover $\omega\varepsilon''$ is always positive except for $\omega=0$ where it is null). This is a result of deep physical meaning: in fact, the quantity $\varepsilon(\mathbf{Q},\omega)$ is the wave-vector- and frequency-dependent dielectric function (the electronic contribution) of the system. Then this quantity has several physical properties, in particular, the product $\omega\varepsilon''(\mathbf{Q},\omega)$ is the absorption coefficient of electromagnetic radiation [45], which is always positive and null only for $\omega=0$. The roots of the real part provide the dispersion relation ω vs $\mathbf{Q}$ of the elementary excitations in the carrier's fluid [44]. The imaginary part times the frequency has a peak at the points where the real part is zero; this reflects the fact that the real and the imaginary parts are not independent, but related by the so-called Kramers–Krönig relations [45], which are a consequence of the principle of causality. Consequently, there are no solutions of Eq. (32) for frequencies different than zero and, then, a complex behavior in time, as a limit cycle, for instance, cannot be expected. Therefore, the system of mobile carriers in the lattice background is stable against time-dependent fluctuations.

However, in the static case ($\omega=0$), the imaginary part of the dielectric function is identically zero for any $\mathbf{Q}$, i.e., $\varepsilon''(\mathbf{Q},0)=0$. Therefore, a stationary spatial ordering can follow for a critical value of the intensity I_c of the pumping source if the real part of the dielectric function becomes zero for certain Q, i.e.,

$$\varepsilon'(\mathbf{Q},0)=1-\mathcal{V}(\mathbf{Q})\sum_{\mathbf{k}}\frac{\mathcal{M}'(\mathbf{k},\mathbf{Q})}{\mathcal{D}(\mathbf{k},\mathbf{Q})}=0, \qquad (38)$$

where $\mathcal{M}'(\mathbf{k},\mathbf{Q})$ and $\mathcal{D}(\mathbf{k},\mathbf{Q})$ are the quantities defined in Eqs. (37a) and (37c), respectively, but evaluated in $\omega=0$.

Therefore, if such root exists for a given I_c at a value $Q=Q_c$, the homogeneous steady state becomes unstable against the emergence of a structure of the form

$$n(z)=n_h-n_e+\frac{1}{2}\{[n_h(Q_c)+n_e(Q_c)]e^{iQ_cz'}+\text{c.c.}\} \qquad (39)$$

(in units of the electronic charge e), where $n_h\gg n_e$. This is a steady-state charge-density wave of wavelength $2\pi/Q_c$ running in the direction of the z axis of the quasi-one-dimensional system, which is superimposed on the homogeneous background with density n_h. At this point (characterized by I_c and Q_c) we have a bifurcation point of solutions, with the solution describing the emergence of the spatial pattern separating out from the so-called thermodynamic solution corresponding to the homogeneous steady state. This is a first bifurcation point: we can think of it as a kind of fork bifurcation, where the branches corresponding to the ordered state, characterized by the amplitude $|n(Q_c)|$, emerges from the so-called thermodynamic branch ($|n(Q)|=0$) at the critical intensity $I=I_c$. Moreover, we anticipate that the first Q_c corresponds to the limit of very long wavelengths, i.e., Q_c going to zero.

The charge-density wave of Eq. (39) is a static (or "frozen") plasma wave, a kind of soft mode that is in the origin of ferroelectricity, antiferroelectricity, and helielectricity in dielectrics (a "frozen" vibrational mode). Therefore, we can consider the emerging structure as a helielectric state or a driven electret state in a biosystem, i.e., a bioelectret [29].

In this case we have an interesting example of emergence of a dissipative structure in Nicolis and Prigogine's sense [4–6]: Coulomb interaction producing collective modes (the plasmons of the microscopic dynamics) and dissipative effects (of macroscopic thermohydrodynamic kinetics) producing thermal disorganization are involved in a "tug of war" towards the production of a macroscopic ordered structure. At low pumping intensities, when the system is near equilibrium (the so-called strictly linear regime of nonequilibrium thermodynamics) morphological ordering cannot be expected because of Prigogine's theorem of minimum entropy production, as it has already been noted. Only in conditions sufficiently away from equilibrium are the nonlinear contributions capable to work against the tendency to disorder (stabilizing a homogeneous state) leading to the emergence of macroscopic ordering; this is discussed in detail in the following section.

III. COMPLEX SPATIAL PATTERN

Before proceeding further, two points have to be taken into account: one is that Q is not a continuous wave number, but takes discrete values because the sample is finite in length. Because of boundary conditions (the wave amplitude is zero at the borders) the possible wave vectors are given by $Q=\ell\pi/L$, where ℓ is an integer ($\ell=1,2,3,...$) and L is the length of the sample. The second point is that Q is bounded

between its lowest possible value π/L and an upper value $\ell_M \pi/L$, because Q must be smaller or at most equal to the Brillouin radius $Q_B = \pi/a$; then ℓ_M is the integer part of L/a (if we take $L = 1$ cm and $a = 100$ Å, then $\ell_M = 10^6$).

Furthermore, once the first bifurcation point at I_c has been reached, for increasing pumping intensity beyond I_c, i.e., for $I > I_c$, we would need to analyze $\varepsilon(\mathbf{Q}, 0)$ after the inhomogeneous state has set in a steady-state condition. This implies a return to Eqs. (21) and to include the nonlinear terms $\mathcal{N}$. However, since the amplitudes $n_a(Q_c)$ contribute quadratically to $\varepsilon(\mathbf{Q}, 0)$ and are very small in the neighborhood of the critical point, we can neglect these terms in a first approximation. Thus, we analyze, for $I > I_c$, the real part of the dielectric function as given by Eq. (38).

We illustrate these results using number characteristics of an α-helix structure in proteins [23]. We take $a \sim 100$ Å, and then $Q_B \sim 3.14 \times 10^6$ cm^{-1}, and n_h will be fixed in the range of $10^5 - 10^6$ cm^{-1}, while the concentration of the thermally excited electrons in the conduction band is much smaller; the hole temperature is fixed at 300 K. For the electron and hole energy dispersion relation we use a parabolic law of the form

$$\varepsilon_{\mathbf{k}}^{h(e)} = \frac{1}{2} \Gamma_{h(e)} a^2 k^2, \tag{40}$$

where $\Gamma_{h(e)}$ is a constant with dimension of energy. In the calculations we take the continuous limit for k, meaning that the summation over k is transformed into an integration of the form

$$\sum_{\mathbf{k}} \rightarrow \frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} dk. \tag{41}$$

Finally, the coupling constants A_{kQ}^e and A_{kQ}^h of Eq. (23) are taken as independent of k and Q and equal to each other without loss of generality ($A_{kQ}^h = A_{kQ}^e = A$).

Because of the singularity in the potential $\mathcal{V}(Q)$ when Q goes to zero, one expects a first root of Eq. (38) for very small values of Q (say the minimum possible value π/L). After performing an expansion of the right-hand side (rhs) of Eqs. (37) in powers of Q around $Q = 0$, we obtain the approximate expressions

$$\mathcal{M}'(\mathbf{k}, \mathbf{Q}) = 2A^2 \beta (\Gamma_h \bar{f}_{\mathbf{k}}^h - \Gamma_e \bar{f}_{\mathbf{k}}^e)(\Gamma_e - \Gamma_h)$$
$$- \beta a^4 (\mathbf{k} \cdot \mathbf{Q})^2 \Gamma_e^2 \Gamma_h^2 (\bar{f}_{\mathbf{k}}^e + \bar{f}_{\mathbf{k}}^h), \tag{42}$$

$$\mathcal{D}(\mathbf{k}, \mathbf{Q}) = A^2 (\Gamma_e - \Gamma_h)^2 + a^4 (\mathbf{k} \cdot \mathbf{Q})^2 \Gamma_e^h \Gamma_h^2, \tag{43}$$

where $\bar{f}_{\mathbf{k}}^e$ and $\bar{f}_{\mathbf{k}}^h$ are the populations given in Eq. (31).

For Eq. (38) to have a root it is necessary that the second term in Eq. (42) be negative. As a rule Γ_e of the conduction band is larger than Γ_h of the valence band and, then, it must be verified that $\Gamma_h \bar{f}_{\mathbf{k}}^h > \Gamma_e \bar{f}_{\mathbf{k}}^e$, which requires that the concentration n_h must be larger than n_e. This is the case in proteins, which are p doped, for a sufficiently large value of A which incorporates the intensity I of the source [cf. Eq. (23)]. For $I = 0$ (then $A = 0$) no zero of $\varepsilon'(\mathbf{Q}, 0)$ is possible. As the intensity I increases, the first instability occurs at the mini-
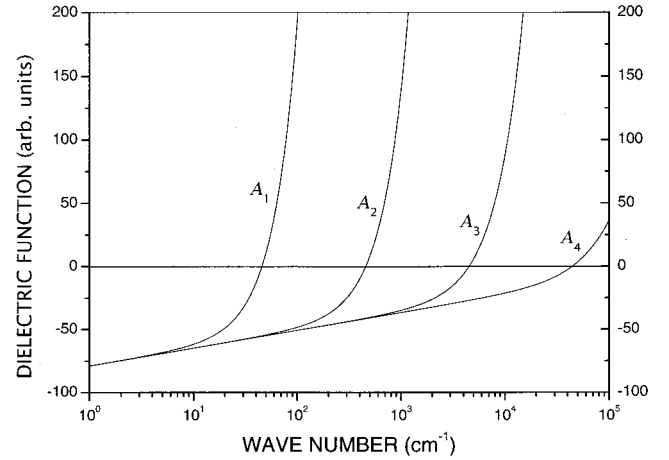

FIG. 1. The real part of the static dielectric function depending on wave number, for several values of the coupling strength, $A_1 = 10^{-18}$, $A_2 = 10^{-17}$, $A_3 = 10^{-16}$, $A_4 = 10^{-15}$ erg. The roots are clearly evidenced, as well as the region where it becomes negative.

mum possible value of Q, namely, $Q_c = \pi/L$; in this case, the critical value of A is $A_c \approx 10^{-20}$ erg for a length $L \approx 1$ cm.

Let us now consider the neighborhood of the first bifurcation at A_c and Q_c. For that purpose we need to obtain the dielectric function in the state, and carry out stability analysis of the first bifurcating branch. For weak-to-moderate intensity above I_c, such that we can neglect in a first approximation the bilinear contributions (leading to mode mixing), the analysis proceeds as in Sec. II above. The homogeneous and steady state of reference is functionally stable, and an instability follows in the presence of additional inhomogeneous fluctuations. Figure 1 shows the real part of the dielectric function for several values of A. We see that, with A increasing beyond A_c, the dielectric function vanishes for values of Q larger than $Q_c = \pi/L$. If for a given A the roots of ϵ' occurs at wave-vectors $Q_l = l\pi/L$, then the instabilities of the homogeneous state follow against sinusoidal waves with wave numbers $\pi/L, 2\pi/L, \ldots, l\pi/L$. Therefore, these modes are contributing to compose the spatial charge density in the system, leading to a structure of the form

$$n(z) = n_h + \sum_{n=1}^{n=l} [n_h(n\pi/L) e^{i(n\pi/L)z} + \text{c.c.}] + n_{\text{NL}}(z), \tag{44}$$

once we disregard the contribution of the dilute gas of electron-type carriers, and where $n_{\text{NL}}(z)$ contains additional terms involving mode mixing, arising out of the nonlinear coupling terms. However, in conditions leading to the emergence of only small amplitudes $n_h(Q)$ (weak-to-moderate pumping intensities), the linear terms would predominate. This suggests that, with increasing intensity I above the critical intensity I_c (corresponding to the first bifurcation), a charge-density wave composed of a large number of normal modes will emerge in the system.

Figure 2 shows the dependence of the critical wave numbers with the coupling intensity A for three different values
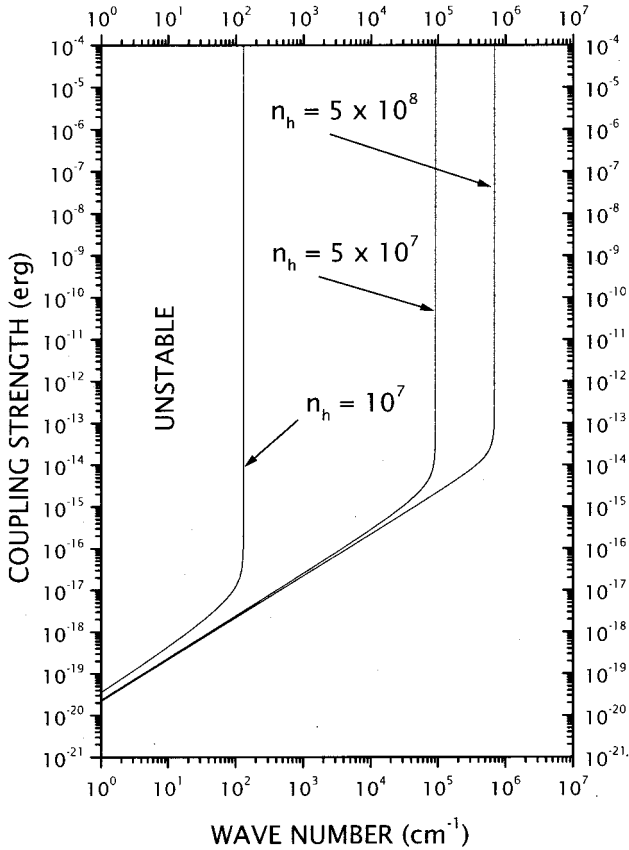
FIG. 2. Linear stability diagram associated with bifurcations of the homogeneous and steady-state solutions, for three values of the hole density (in cm^{-1}). First instability occurs in the limit $Q \rightarrow 0$, where the minimum of the marginal stability is located.

of the hole concentration; the range of values of Q contributing to the formation of the spatial structure increases with increasing doping, but in all cases tends to a limiting value.

We end this section with considerations of a general character. First we notice that, from the physical point of view, the bifurcation point corresponds to a zero of the static dielectric function for a certain wave number. Therefore, for those wave numbers the so-called dielectric response function $\varepsilon^{-1}(\mathbf{Q},0)$ becomes infinite, indicating an instability of the homogeneous charge density against the formation of an organized structure. This has a complete analogy with the criteria of phase transitions in equilibrium. In fact, in the latter case, the critical (or transition) point is characterized by a singularity in a particular physical property, for example, an infinite value of the specific heat in changes of structure, an infinite value of the magnetic susceptibility in a ferromagnetic transition, etc. In the first case just mentione we have $\Delta Q = C \Delta T$, by definition of the specific heat C, where ΔQ is the heat provided to the sample and ΔT the change in temperature. In this case C goes to infinity in the transition point and, since ΔQ is finite, the temperature remains constant as the transition proceeds. In the second case mentioned above, the magnetic displacement vector and magnetic field are related by $\mathbf{B} = \mu \mathbf{H}$ and then as the magnetic permeability μ goes to infinity, the magnetic displacement vector van-

ishes; therefore, since $\mathbf{B} = -4 \pi \mathbf{M}$, a spontaneous ferromagnetization $\mathbf{M} \neq \mathbf{0}$ must emerge [46].

Consider now the case of nonequilibrium systems arbitrarily away from equilibrium. We can introduce ideas that have a close analogy with the case of phase transitions, but keeping in mind that the role of phases in equilibrium is now played by the stationary dissipative structure. For the carriers' system described here, since the electric field is $\mathbf{E}(\mathbf{Q}) = \varepsilon^{-1}(\mathbf{Q},0)\mathbf{D}(\mathbf{Q})$, when ε^{-1} goes to infinity the electric displacement vector $\mathbf{D}(\mathbf{Q})$ must be zero. Therefore, the relation $\mathbf{D}(\mathbf{Q}) = \mathbf{E}(\mathbf{Q}) + 4 \pi \mathbf{P}(\mathbf{Q})$ implies in the emergence of a spontaneous and space-dependent electric polarization $\mathbf{P} \neq \mathbf{0}$, namely, the charge-density wave we have evidenced. This is similar to the case of electrical polarizable phase transitions in equilibrium, with $\mathbf{Q} = \mathbf{0}$ for ferroelectrics, $|\mathbf{Q}| = \pi/a$ for antiferroelectrics (a is the lattice parameter in the direction of $\mathbf{Q}$), and arbitrary $\mathbf{Q}$ for helical-electrical materials.

After the first and following bifurcations have occurred, the spatially ordered state consists of a complicated structure, containing the linear superposition of modes as in Eq. (44) plus nonlinear contributions (not shown). This leads us to the prediction of a particular asymptotic phenomenon where the growing number of normal modes (with ever increasing l), interacting together to compose the local density $n_h(z)$, would lead to an excess of modes in the system. It is worth noting the analogy with Landau's theory of turbulence [47], but with the difference that in the latter case there is an overexcess of frequency-dependent oscillations (so it is a time-dependent problem), while here there is an overexcess of steady-state space-varying modes (a space-dependent problem).

IV. THERMODYNAMIC ANALYSIS OF THE MORPHOLOGICAL TRANSITION

Given initial conditions the complete evolution of the nonequilibrium-dissipative macroscopic state of the system is determined by solving Eqs. (19) and (20). The initial conditions in this case refer to the initial preparation of the system near or far away from equilibrium.

The dissipative character of the set of equations is reflected in that, when embedding the equations of evolution into the space of the nonequilibrium thermodynamic space defined by the set of variables of Eq. (10), a contraction of an element of volume is obtained, each point of which follows the evolution laws. This very important property can be expressed by an inequality [48,49], which in the present case is given by

$$\frac{1}{t-t_0} \int_{t_0}^{t} dt' \operatorname{div} \sum_a \mathbf{\Phi}^a(Q,t') < 0, \qquad (45)$$

where

$$\operatorname{div} \sum_a \mathbf{\Phi}^a(Q,t') = \sum_a \sum_k \frac{\delta}{\delta n_{\mathbf{kQ}}^a(t)} \mathbf{\Phi}_{\mathbf{kQ}}^a(t), \qquad (46)$$

and δ stands for functional derivative [50]. Using Eqs. (21) we obtain that

$$\frac{\delta}{\delta n_{\mathbf{kQ}}^e(t)} \Phi_{\mathbf{kQ}}^e = -\frac{1}{i\hbar} E_{\mathbf{kQ}}^e + \frac{1}{i\hbar} \mathcal{V}(\mathbf{Q}) \Delta f_{\mathbf{kQ}}^e + A_{\mathbf{kQ}}^e,$$

(47a)

$$\frac{\delta}{\delta n_{\mathbf{kQ}}^e(t)} \Phi_{\mathbf{kQ}}^h = \frac{1}{i\hbar} E_{\mathbf{kQ}}^e - \frac{1}{i\hbar} \mathcal{V}(\mathbf{Q}) \Delta f_{\mathbf{kQ}}^e + A_{\mathbf{kQ}}^h. \quad (47b)$$

In Eqs. (47) the contributions from $\mathcal{R}$ and $\mathcal{N}$ have been disregarded since $\mathcal{N}$ is quadratic in the amplitudes and the effect of the phonons in $\mathcal{R}$ is small when compared to the magnitude of A, which is proportional to the source intensity. Next, summing Eqs. (47) over $\mathbf{k}$, and using Eq. (46) we have

$$\text{div } \mathbf{\Phi}^a(\mathbf{Q}, t) \simeq -\sum_k A_{\mathbf{kQ}}^a. \tag{48}$$

Since the coefficients A are positive, the divergence in Eq. (48) is negative and, then, the quantity within the integral in Eq. (45) is always negative and the inequality is verified.

To study the thermodynamical aspects of the problem we introduce the informational entropy in MaxEnt-NESOM-based IST [10–13], in this case given by

$$\bar{S}(t) = -\text{Tr}\{\varrho_\varepsilon(t)\hat{S}(t,0)\} = \phi(t) + \bar{S}_u + \sum_{\mathbf{kQ}a} F_{\mathbf{kQ}}^a(t) n_{\mathbf{kQ}}^a(t).$$

(49)

In Eq. (49), we have separated out the contributions from the homogeneous part, $\bar{S}_u$ (corresponding to the variables E_c, n_h, n_h, and E_L), from those of the inhomogeneous part (corresponding to the amplitudes $n_{\mathbf{kQ}}^a$).

First let us calculate the average values of the quantities $\hat{n}_{\mathbf{kQ}}^a$ in terms of their associated multipliers, $F_{\mathbf{kQ}}^a(t)$, that is,

$$n_{\mathbf{kQ}}^a(t) = \text{Tr}\{\hat{n}_{\mathbf{kQ}}^a \varrho_\varepsilon(t)\} = \text{Tr}\{\hat{n}_{\mathbf{kQ}}^a \bar{\varrho}(t)\}, \tag{50}$$

which are calculated using Heims-Jaynes perturbation expansion for averages [51]; in a *linear approximation* in the Lagrange multipliers $F_{\mathbf{kQ}}$ we obtain

$$n_{\mathbf{kQ}}^a = M_{\mathbf{kQ}}^a F_{\mathbf{kQ}}^a(t), \tag{51}$$

with

$$M_{\mathbf{kQ}}^a = \frac{\Delta \bar{f}_{\mathbf{kQ}}^a}{\beta E_{\mathbf{kQ}}^a} \simeq \frac{\mathbf{Q} \cdot \nabla_k \bar{f}_{\mathbf{kQ}}^a}{\beta \mathbf{Q} \cdot \nabla_k \epsilon_k^a} = \frac{\mathbf{Q} \cdot \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}}{\beta \mathbf{Q} \cdot \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}} \frac{\partial \bar{f}_{\mathbf{kQ}}^a}{\partial \epsilon_{\mathbf{kQ}}^a}$$

$$= k_B T_c^* \frac{\partial \bar{f}_{\mathbf{kQ}}^a}{\partial \epsilon_{\mathbf{kQ}}^a} \tag{52}$$

calculated in the limit of small Q. Equation (52) is time independent because of the assumed stationary character of the homogeneous state, i.e., β and μ are constant in time. We recall that $F_{\mathbf{kQ}}^a(t) = \delta \bar{S}(t) / \delta n_{\mathbf{kQ}}^a(t)$ which, along with the relations $\delta \bar{S}(t) / \delta E_c = \beta$ and $\delta \bar{S}(t) / \delta N = -\beta \mu$, constitute the nonequilibrium equations of state in IST.

We can now study the contribution of the morphological transition to the informational entropy in IST. This is done in terms of the quantity

$$\Omega = \frac{\Delta \bar{S}}{\bar{S}_0^{\text{ss}}} = \frac{\bar{S}_0^{\text{ss}} - \bar{S}^{\text{ss}}}{\bar{S}_0^{\text{ss}}} = -\sum_{\mathbf{kQ}a} F_{\mathbf{kQ}}^{a(\text{ss})} n_{\mathbf{kQ}}^{a(\text{ss})} = -\sum_{\mathbf{kQ}a} M_{\mathbf{kQ}}^a |F_{\mathbf{kQ}}^{a(\text{ss})}|^2$$

$$= -\sum_{\mathbf{kQ}a} [M_{\mathbf{kQ}}^a]^{-1} |n_{\mathbf{kQ}}^{a(\text{ss})}|^2, \tag{53}$$

obtained after using Eq. (51). In Eq. (53) $\bar{S}_0^{\text{ss}}$ is the informational entropy of the homogeneous state in the absence of the nonhomogeneous contribution, while $\bar{S}^{\text{ss}}$ is the informational entropy in the presence of the spatial ordering, both taken in the steady state.

The quantity Ω plays the role of a Kullback-like order parameter [52], which is a positive quantity since M is negative for nonzero $n_{\mathbf{kQ}}^h$ [$\partial f / \partial \epsilon < 0$ in Eq. (52), because the populations decrease with increasing energies]. This implies that $\bar{S} < \bar{S}_0$, indicating that the informational entropy decreases as the amplitude of the charge-density wave increases with increasing intensity beyond the critical value.

Let us consider the immediate neighborhood of the first bifurcation. Using Eqs. (28) in the steady state (ss), i.e., $\omega = 0$, we obtain a linear relation between the individual amplitudes $n_{\mathbf{kQ}}^a$ and the wave amplitude $n^a(\mathbf{Q})$, namely,

$$n_{\mathbf{kQ}}^{a(\text{ss})} \simeq C_{\mathbf{kQ}}^a n^{a(\text{ss})}(\mathbf{Q}), \tag{54}$$

where

$$n_{\mathbf{k}}^{a(\text{ss})}(\mathbf{Q}) = \sum_{\mathbf{k}} n_{\mathbf{kQ}}^{a(\text{ss})}, \tag{55}$$

$$C_{\mathbf{kQ}}^a = \mathcal{V}(\mathbf{Q}) \sum_{\mathbf{k}} \frac{\bar{f}_{\mathbf{k}+1/2\mathbf{Q}}^a - \bar{f}_{\mathbf{k}-1/2\mathbf{Q}}^a}{\varepsilon_{\mathbf{k}+1/2\mathbf{Q}}^a - \varepsilon_{\mathbf{k}-1/2\mathbf{Q}}^a + iA_{\mathbf{kQ}}^a}. \tag{56}$$

Using these results, after some algebra we find that

$$\Delta \bar{S}^{(\text{ss})} = G(\mathbf{Q}) |n^{\text{ss}}(\mathbf{Q})|^2 \sim \left[\frac{I}{I_c} - 1\right]^{1/2}, \tag{57}$$

once we take $A_{\mathbf{kQ}}^a = A = \lambda I$ [cf. Eq. (23)], and where

$$G(\mathbf{Q}) = -\sum_{\mathbf{k}a} M_{\mathbf{kQ}}^a |C_{\mathbf{kQ}}^a|^2, \tag{58}$$

$$n^{(\text{ss})}(\mathbf{Q}) = \sum_a n^{a(\text{ss})}(\mathbf{Q}). \tag{59}$$

Equation (57) implies that, in the immediate neighborhood of the first bifurcation, the order parameter Ω of Eq. (53) increases with the pumping intensity following a square-root law. This result has a strong resemblance with the square-root law for the order parameter in Landau's theory of second-order phase transitions [46].

We consider next the global informational-entropy production in IST, which gives relevant information on the dissipative behavior of the system. This nonequilibrium thermodynamic function is given by

$$\bar{\sigma}(t) = \frac{d}{dt}\bar{S}(t) = \frac{d}{dt}S_u(t) + \sum_{\mathbf{kQ}a} F^a_{\mathbf{kQ}}(t)\frac{d}{dt}n^a_{\mathbf{kQ}}(t)$$

$$\simeq \sum_{\mathbf{kQ}a} F^a_{\mathbf{kQ}}(t)\Phi^a_{\mathbf{kQ}}(t), \tag{60}$$

where we have used that $dS_u(t)/dt \simeq 0$ along with Eqs. (19) and (20), and then it depends almost exclusively on the inhomogeneous variables. The informational-entropy production can be decomposed in two terms in the form

$$\bar{\sigma}(t) = \bar{\sigma}_{(i)} + \bar{\sigma}_{(e)}, \tag{61}$$

where $\bar{\sigma}_{(i)}$ is the internal contribution, which results from the internal interactions in the system, and $\bar{\sigma}_{(e)}$ is the external contribution, due to interactions with the surrounding. We note that in the limiting case when the theory describes the restricted classical irreversible thermodynamics (when local equilibrium is assumed), the quantity $\bar{\sigma}_{(i)}$ becomes simply the entropy production. In equilibrium and in local equilibrium, the informational entropy coincides with the definition given by Clausius. In the linear domain of irreversible thermodynamics the theorem of minimum entropy production excludes the possibility of macroscopic ordering (it is the domain of the thermal chaos); as already pointed out, complexity of the type described here, requires nonlinear contributions in the kinetic equations and an accompanying breaking of Onsager's symmetry relations [11,12].

Considering the steady state, where $\bar{\sigma}^{\mathrm{ss}} = 0$ and then $\bar{\sigma}^{\mathrm{ss}}_{(i)} = -\sigma^{\mathrm{ss}}_{(e)}$ and using Eqs. (51) and (54), we can write the different contributions in the form

$$\bar{\sigma}^{\mathrm{ss}}_{(i)} = \frac{1}{i\hbar}\sum_{\mathbf{kQ}a} |\mathcal{V}(\mathbf{Q})|^2 (f^a_{\mathbf{k}+1/2\mathbf{Q}} - f^a_{\mathbf{k}+1/2\mathbf{Q}})|C^a_{\mathbf{kQ}}|^2 |n^{\mathrm{ss}}(\mathbf{Q})|^2, \tag{62}$$

$$\bar{\sigma}^{(\mathrm{ss})}_{(e)} = \sum_{\mathbf{kQ}} A_{\mathbf{kQ}}[M^{\mathrm{ss}}_{\mathbf{kQ}a}]^{-1}|C^a_{\mathbf{kQ}}|^2 |n^{\mathrm{ss}}(\mathbf{Q})|^2. \tag{63}$$

If we change $\mathbf{Q}$ by $-\mathbf{Q}$ and note that $C_{\mathbf{k},-\mathbf{Q}} = C^*_{\mathbf{kQ}}$ and $M_{\mathbf{k},-\mathbf{Q}} = M^*_{\mathbf{kQ}}$ (asterisks indicate complex conjugate) we obtain that both $\bar{\sigma}$'s in Eqs. (62) and (63) are real quantities. Furthermore, the external production of informational entropy is negative [$M < 0$; cf. Eq. (52)], meaning that informational entropy is pumped out of the system, while the internal contribution is positive, which can be considered a manifestation of the second law of thermodynamics. We recall that the informational entropy in IST satisfies an $\mathcal{H}$ theorem, that we have called a weak principle of increase of informational-statistical entropy [11–13].

Two other important nonequilibrium thermodynamic functions are: (a) the rate of change of the informational-entropy production due to the change in time of the Lagrange

multipliers (or intensive nonequilibrium thermodynamic variables), which is given in this case by

$$\frac{d_F\bar{\sigma}(t)}{dt} = \sum_{\mathbf{kQ}a} \frac{d}{dt}F^a_{\mathbf{kQ}}(t)\frac{d}{dt}n^a_{\mathbf{kQ}}(t)$$

$$= \sum_{\mathbf{kQ}a} [M_{\mathbf{kQ}a}]^{-1}\frac{d}{dt}n^{a*}_{\mathbf{kQ}}(t)\frac{d}{dt}n^a_{\mathbf{kQ}}(t)$$

$$= \sum_{\mathbf{kQ}a} [M_{\mathbf{kQ}a}]^{-1}|\Phi^a_{\mathbf{kQ}}(t)|^2, \tag{64}$$

and (b) the rate of change due to the change in time of the macrovariables, that is,

$$\frac{d_Q\bar{\sigma}(t)}{dt} = \sum_{\mathbf{kQ}a} F^a_{\mathbf{kQ}}(t)\frac{d^2}{dt^2}n^a_{\mathbf{kQ}}$$

$$\simeq \sum_{\mathbf{kQ}} a \, [M_{\mathbf{kQ}a}]^{-1}n^a_{\mathbf{kQ}}\frac{d}{dt}\Phi^a_{\mathbf{kQ}}(t). \tag{65}$$

The quantity of Eq. (64) is negative [$M < 0$; cf. Eq. (52)], as it should, since this result is a manifestation of the theorem of evolution in IST [12], a generalization of the thermodynamic principle of evolution of Glansdorff-Prigogine [6,53]. This principle states that along the trajectories in the thermodynamic space of states, governed by the MaxEnt-NESOM kinetic equations [Eqs. (19) and (20) in the present case], the rate of change in time of the informational-entropy production resulting from the rate of change of the Lagrange multipliers must be a negative quantity.

We turn now to the question of the stability of the charge-density wave. Linear stability analysis in Lyapunov style is the mathematical way, but an alternative and equivalent approach with physical meaning is the (in)stability criterion in IST [12], which is a generalization of the Glansdorff-Prigogine criterion [6,53] in nonlinear classical thermodynamics. It states that a solution (structure) is stable when two thermodynamic functions have the opposite sign: One of these functions is $\delta\bar{S}$, which, after using Eqs. (49) and (51), is given by

$$\delta\bar{S}(t) = \sum_{\mathbf{kQ}a} C^{(\mathrm{ss})}_{\mathbf{kQ}a}|\delta n^a_{\mathbf{kQ}}(t)|^2 > 0, \tag{66}$$

where δn stands for an arbitrary small change in the basic variable $n^a_{\mathbf{kQ}}$ from its value in the steady state. The other quantity is the second functional derivative of the informational entropy taken in the steady state, i.e.,

$$C^{(\mathrm{ss})}_{\mathbf{kQ}a} = \frac{\delta^2\bar{S}}{\delta^2 n^a_{\mathbf{kQ}}}\bigg]^{\mathrm{ss}}. \tag{67}$$

The positiveness of the rhs Eq. (66) is a consequence that it is a manifestation of the curvature of the informational entropy in the steady state, which is a maximum because of MaxEnt. The quantity defined in Eq. (67) is the change in time of the informational entropy, namely,

$$\frac{d}{dt}\frac{1}{2}\delta\bar{S}(t) = \sum_{\mathbf{kQ}a} C^{(\text{ss})}_{\mathbf{kQ}a}\frac{d}{dt}|\delta n^a_{\mathbf{kQ}}(t)|^2$$

$$= \sum_{\mathbf{kQ}a} C^{(\text{ss})}_{\mathbf{kQ}a}\left[\delta n^a_{\mathbf{kQ}}(t)\frac{d}{dt}\delta n^{a*}_{\mathbf{kQ}}(t)\right.$$

$$\left. + \delta n^{a*}_{\mathbf{kQ}}(t)\frac{d}{dt}\delta n^a_{\mathbf{kQ}}(t)\right]$$

$$= \sum_{\mathbf{kQ}a} C^{(\text{ss})}_{\mathbf{kQ}a}[\delta n^a_{\mathbf{kQ}}(t)\Phi^*_{\mathbf{kQ}}(t) + \delta n^{a*}_{\mathbf{kQ}}(t)\Phi^a_{\mathbf{kQ}}(t)]$$

$$= -\sum_{\mathbf{kQ}a} C^{(\text{ss})}_{\mathbf{kQ}a}A^a_{\mathbf{kQ}}|\delta n^a_{\mathbf{kQ}}(t)|^2, \qquad (68)$$

once we use the equations of evolution, Eqs. (19) and (20), after neglecting the terms with $\mathcal{R}$ and $\mathcal{N}$, and taking into account that $dn^a_{\mathbf{kQ}}/dt = d(n^{a(\text{ss})}_{\mathbf{kQ}} + \delta n^a_{\mathbf{kQ}})/dt = d\delta n^a_{\mathbf{kQ}}/dt$. The quantity defined in Eq. (68) is also negative, and then, according to the (in)stability theorem, the organized state of charge density waves is stable with respect to the homogeneous stationary state.

Note that the quantity of Eq. (68) is the so-called excess entropy production function, which measures the difference between the informational-entropy production in the displaced state, by δn, and that in the steady state.

V. CONCLUSIONS

We have evidenced the possible emergence of morphological ordering in the form of static charge-density waves in the carrier's system of biopolymers, as the α-helix secondary structure in proteins. This is a kind of dissipative structure in Prigogine's sense, which is only possible in systems governed by nonlinear kinetic equations and when driven sufficiently far from equilibrium, outside the linear regime of classical thermodynamics. Ordered states in the latter regime are excluded because of Prigogine's theorem of minimum entropy production. Self-organization can only arise when Onsager's reciprocal relations (strictly valid in the linear regime around equilibrium) are violated, what is possible only in the nonlinear domain.

In the present case the spatial organization is a consequence of the organizing effects forced by Coulomb interaction between the carriers, responsible for their collective motion in the form of plasma waves. We can say that the emergence of the organized static charge-density waves is a consequence of the formation of steady states of plasma

waves (kind of "frozen" plasmons). In the interplay between the organizing Coulomb interaction and dissipative effects working to lead the system to disorganized thermal chaos, the former overcomes the latter at a certain threshold of intensity of the external pumping source. This happens when the system is sufficiently far from equilibrium and nonlinear effects become strong enough compared with relaxation (dissipative) effects.

In Sec. IV, we have described some properties of this dynamical system, like the contraction of a volume element in the thermodynamic Gibbs space, each point of it following the equations of evolution, what evidences the overall dissipative character of the dynamics. We notice that only part of the pumped energy is redirected to the formation of order instead of being wasted out in thermal motion. Moreover, the morphological transition has been characterized by an order parameter [cf. Eq. (53)], which has the interesting property given in Eq. (57), which resembles the behavior of the order parameter in Landau's theory of second-order phase transitions. This is expected since we have used a mean-field theory in a many-body system.

Nonequilibrium thermodynamic properties have also been considered, as the production of informational-statistical entropy, and its separation in internal and external contributions. The principle of evolution has been also verified, and the stability of the ordered space against the homogeneous state. The internal production of informational-statistical entropy is positive, which is a manifestation of an $\mathcal{H}$ theorem, further reinforcing the dissipative character of the equations of evolution.

As final words, we recall A. Szent-Györgyi and McLaughlin's arguments that organization of electrons (as mobile carriers) in living matter may have biological consequences. The present paper has stressed that such ordering is possible as a result of biological systems being open systems working in far-from-equilibrium conditions.

[1] P. W. Anderson, Science **177**, 393 (1972).

[2] P. W. Anderson, Phys. Today **44**(7), 9 (1991).

[3] M. Gell-Mann, Complexity **1**, 16 (1995).

[4] I. Prigogine, in *From Theoretical Physics to Biology*, edited by M. Marois (North-Holland, Amsterdam, 1969).

[5] G. Nicolis and I. Prigogine, *Exploring Complexity* (Freeman, New York, 1989).

[6] G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley-Interscience, New York, 1977).

[7] A. M. Turing, Philos. Trans. R. Soc. London, Ser. B **232**, 37 (1952).

[8] G. Nicolis, Physica A **213**, 1 (1995).

[9] A. Hobson, J. Chem. Phys. **45**, 1352 (1966).

[10] L. S. García-Colín, A. R. Vasconcellos, and R. Luzzi, J. Non-

Equilib. Thermodyn. **19**, 24 (1994).

[11] R. Luzzi, A. R. Vasconcellos, and J. G. Ramos, *Statistical Foundations of Irreversible Thermodynamics* (Teubner Bertelsmann-Springer, Stuttgart, 2000).

[12] M. A. Tenan, A. R. Vasconcellos, and R. Luzzi, Fortschr. Phys. **45**, 1 (1997).

[13] R. Luzzi, A. R. Vasconcellos, and J. G. Ramos, Fortschr. Phys. **47**, 401 (1999).

[14] D. N. Zubarev, *Neravnovesnaia Statisticheskaia Termodinamika* (Izd. Nauka, Moscow, 1971) [*Nonequilibrium Statistical Thermodynamics* (Consultants Bureau, New York, 1974)].

[15] D. N. Zubarev, V. N. Morozov, and G. Röpke, *Statistical Mechanics of Nonequilibrium Processes. Vol. 1: Basic Concepts, Kinetic Theory; Vol. 2: Relaxation and Hydrodynamic Processes* (Akademie Verlag-Wiley VCH, Berlin, 1996).

[16] R. Luzzi and A. R. Vasconcellos, Fortschr. Phys. **38**, 887 (1990).

[17] J. G. Ramos, A. R. Vasconcellos, and R. Luzzi, Fortschr. Phys. **43**, 265 (1995).

[18] E. T. Jaynes, articles and notes in *E. T. Jaynes Papers on Probability, Statistics, and Statistical Physics*, edited by R. D. Rosenkrantz (Reidel, Dordrecht, 1983).

[19] A. I. Akhiezer and S. V. Peletminskii, *Methods of Statistical Physics* (Pergamon, Oxford, 1981).

[20] L. Lauck, A. R. Vasconcellos, and R. Luzzi, Physica A **168**, 789 (1990).

[21] R. Luzzi and A. R. Vasconcellos, Complexity **2**, 42 (1997).

[22] S. A. Hassan, A. R. Vasconcellos, and R. Luzzi, Eur. Phys. J. B. **13**, 131 (2000).

[23] A. S. Davydov, *Biology and Quantum Mechanics* (Pergamon, Oxford, 1982).

[24] A. J. Heger, S. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[25] A. R. Vasconcellos, M. V. Mesquita, and R. Luzzi, Phys. Rev. Lett. **80**, 2008 (1998).

[26] R. Pethig, Int. J. Quantum Chem., Quantum Biol. Symp. **5**, 385 (1978).

[27] See, for example, *Chemical and Biological Generation of Excited States*, edited by W. Adam and G. Cilento (Academic, New York, 1982).

[28] A. Szent-Györgyi and J. A. McLaughlin, Int. J. Quantum Chem., Quantum Biol. Symp. **5**, 137 (1978).

[29] S. Mascarenhas, in *Electrets*, edited by G. M. Sessler, (Springer, Berlin, 1987), pp. 321–346.

[30] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1990).

[31] J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 1960).

[32] N. W. Aschroft and N. D. Mermin, *Solid State Physics* (Holt, Reinhart, and Winston, New York, 1976).

[33] D. Pines and P. Nozieres, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).

[34] A. R. Vasconcellos, A. C. Algarte, and R. Luzzi, Physica A **166**, 517 (1990).

[35] A. C. Algarte, A. R. Vasconcellos, and R. Luzzi, Phys. Status Solidi B **173**, 487 (1992).

[36] A. R. Vasconcellos, A. C. Algarte, and R. Luzzi, Phys. Rev. B **48**, 10873 (1995).

[37] S. Hassan, A. R. Vasconcellos, and R. Luzzi, Physica A **262**, 359 (1999).

[38] R. Luzzi, A. R. Vasconcellos, and J. G. Ramos (unpublished); e-print in URL: http://xxx.lanl.gov/abs/cond-mat/9909160.

[39] R. Luzzi, A. R. Vasconcellos, J. Casas-Vazquez, and D. Jou, Physica A **234**, 699 (1997).

[40] R. Luzzi, A. R. Vasconcellos, J. Casas-Vazquez, and D. Jou, J. Chem. Phys. **107**, 7383 (1997).

[41] J. R. Madureira, A. R. Vasconcellos, R. Luzzi, and L. Lauck, Phys. Rev. E **57**, 3637 (1998).

[42] E. B. Davies, Commun. Math. Phys. **34**, 91 (1974).

[43] J. R. Madureira, A. R. Vasconcellos, R. Luzzi, J. Casas-Vazquez, and D. Jou, J. Chem. Phys. **108**, 7568 (1998).

[44] D. Pines, *Elementary Excitations in Solids: Lectures on Phonons, Electrons and Plasmons* (Benjamin, New York, 1964).

[45] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960).

[46] H. E. Stanley, *Introduction to Phase Transition and Critical Phenomena* (Clarendon, Oxford, 1971).

[47] L. D. Landau, Dokl. Akad. Nauk **44**, 339 (1936); also in *Collected Papers of L. D. Landau,* edited by D. ter Haar (Gordon and Breach, New York, 1965).

[48] G. Nicolis, *Introduction to Nonlinear Science* (Cambridge University Press, Cambridge, 1995).

[49] G. Nicolis and D. Daems, Chaos **8**, 311 (1998).

[50] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Wiley-Interscience, New York, 1953), Vol. I, pp. 184–186.

[51] S. P. Heims and E. T. Jaynes, Rev. Mod. Phys. **34**, 143 (1962); Subsection b, pp. 148–150, and Appendix B, p. 164 [it should be noticed that there is a misprint in the third line of their Eq. (B1) which must end in x^{n-1}].

[52] S. Kullback, *Information Theory and Statistics* (Wiley, New York, 1959).

[53] P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability, and Fluctuations* (Wiley-Interscience, New York, 1971).