Symmetry breaking instabilities in illuminated systems*

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Chemically nonreactive and reactive systems (closed and homogeneous) are shown to become unstable to inhomogeneous perturbations beyond given critical intensities of uniform illumination, so that macroscopic inhomogeneities (spatial patterns) arise. We classify symmetry-breaking instabilities into two types: extrinsic length scaling, in which the characteristic length of the developing spatial pattern is determined by the dimensions of the system; and intrinsic length scaling, in which that characteristic length is determined by the dynamics of the system (reaction rates and transport relations). We analyze a variety of nonlinear systems by means of a linear stability analysis. In an illuminated, isothermal, isobaric, two-species system, only extrinsic length scaling is possible; more degrees of freedom, either with increasing number of species or other state variables, are required for intrinsic scaling in the closed system. Next we consider a two-component nonreactive illuminated gaseous system in which diffusion, thermal conduction, and thermal diffusion may occur. We show that if only one component in a thermal diffusion experiment tends towards the hotter region, then extrinsic symmetry-breaking instability is possible. If, in addition, the two species are coupled by reaction (interconversion), then the spatial patterns at the onset of instability are of the intrinsic type. We then include pressure fluctuations in an analysis of a one-component system under steady illumination at a wavelength that is absorbed by the molecules and then converted into heat. We show that such a system may generate and amplify sound waves; that is, the system becomes unstable to spatially periodic pressure (acoustic) variation. This process may be used for the measurement of vibration–translation relaxation rates.

I. INTRODUCTION

We study the instability of uniformly illuminated, closed, homogeneous, nonreactive and reactive systems to the spontaneous onset of macroscopic inhomogeneities, that is to spatial patterning. Instabilities in chemically reacting systems open to mass flux have been analyzed for a variety of problems and from a number of points of view.[1-6] The systems considered here are open only to fluxes of light and heat and are thus closed but nonisolated.

Instability phenomena in illuminated systems have been shown to exist under various conditions. The most familiar examples are maser and laser systems where a positive feedback mechanism is provided by the "autocatalytic" nature of stimulated emission.[7] Other feedback mechanisms in optical systems of this type may be provided by a nonlinear medium; laser oscillations have been interpreted as limit cycles arising from the nonlinear interaction of such a medium with the photon field.[8] In these systems, the essential feedback mechanism and the accompanying nonlinearity are explicitly involved in the interaction of light with matter. In addition, instabilities may occur in systems interacting linearly with light if essential nonlinearities arise from nonoptical processes. This is the case in certain photoconductors, where light is used to produce a nonequilibrium concentration of carriers while feedback and accompanying nonlinearity arise from the electric field dependence of the rate of capture of these carriers.[9] For closed chemical systems, the absorption of light by one component of a chemically reacting system may lead to various instability phenomena.[10] Here again, the interaction of light with the system is linear; the feedback arises from nonlinear rate processes due to, e.g., temperature dependent rate coefficients.

In this work, we study a variety of closed systems that are driven far from equilibrium by composition dependent absorption of homogeneous illumination and that may, as a result, exhibit various instabilities. We demonstrate the onset of instability for the various systems by considering the linearized dynamics describing the evolution of small perturbations from a homogeneous steady state. Some general remarks are made in Sec. II on the classification of symmetry-breaking instabilities into two types, according to whether the length associated with the onset of spatial patterning is fixed by the dimensions of the container, *extrinsic length scaling*, or is imbedded in the transport and reaction kinetics itself, *intrinsic length scaling*. In Sec. III, we show that in a closed isothermal, isobaric illuminated two-species reacting–diffusing system, symmetry breaking can occur only with extrinsic length scaling. Intrinsic symmetry breaking requires three or more species in such systems. In Sec. IV, we consider a two-component, nonisothermal illuminated system. The radiation wavelength is chosen so that light is absorbed by one of the components and is converted into heat by a fast radiationless relaxation process. Spatial structure of the extrinsic type may be spontaneously generated in this system provided that the absorber tends, by thermal diffusion, towards hotter regions. When the two components may be converted into each other by a chemical reaction, an intrinsically scaled spatial structure may result. In Sec. V, we consider a single-component gaseous system that absorbs light by optical (electronic or vibrational) excitation and converts it into heat by radiationless relaxation. We show that under stated conditions such a system may become unstable to spatially periodic pressure variations in the form of sound waves. Sound may be thus amplified or spontaneously generated in this system. We conclude with some remarks and note some possible applications.

II. EXTRINSIC AND INTRINSIC LENGTH SCALING

A qualitative distinction may be made between two types of symmetry breaking based on the pattern length of perturbations to which the system becomes unstable. As the system subject to instability is driven out of equilibrium, symmetry breaking first occurs on a given length scale. If that length is fixed by the dimensions of a given system of arbitrary length, then the symmetry breaking is classified as extrinsic length scaling. In contrast, however, there are systems for which the pattern length, at which symmetry breaking sets in, is essentially independent of the dimensions above a minimal length. In such cases, the *intrinsic* length scaling is embedded in the transport and reaction dynamics. From an operational point of view, the size of the system chosen to test the character of the length scaling must be greater than the intrinsic length. As the intrinsic length approaches infinity, the distinction between the two types of length scaling vanishes.

The onset of instability to small perturbations is found by a linear stability analysis. Consider the evolution of small deviations $\delta\psi$ of the local descriptive variables (concentrations, temperature, pressure, etc.) from their steady state values. For a system under homogeneous constraints, perturbations $\delta\psi(k, t)$ of wave vector k obey the equation

$$\frac{\partial \delta\psi}{\partial t} = \mathbf{M}(k)\delta\psi , \qquad (\text{II.1})$$

where $\mathbf{M}(k)$ is the matrix of the linearized dynamics. If one of the eigenvalues $z(k)$ of $\mathbf{M}(k)$ has a positive real part for some values of k, then the corresponding perturbations at these wave vectors will grow.[11] In Fig. 1, we show a typical k dependence of a branch $z(k)$ of the eigenvalue spectrum for various values of an external constraint, such as light intensity I, which drives and maintains the system out of equilibrium. Because of the dissipative transport processes such as diffusion, thermal conduction, and viscosity, $z(k)$ must approach $-\infty$ as $k \to \infty$. In Fig. 1(a), we see a schematic plot of $z(k)$ for various values of I. For the root shown, the real part is zero at $k = 0$. As I is increased above a critical value I_c, there is a finite interval

$$0 < k < k_m(I) , \qquad (\text{II.2})$$

for which $\text{Re} z(k) > 0$. For this class of systems, k_m increases from zero at I_c,

$$k_m(I_c) = 0 , \qquad (\text{II.3})$$

as I is increased, and it may reach the minimum value π/l available to the system contained in a tube of length l. At this value of the constraint (light intensity), $I = I_e$,

$$k_m(I_e) = \frac{\pi}{l} , \qquad (\text{II.4})$$

the system of length l just becomes unstable. The initial pattern length is thus that of the container. Symmetry breaking takes place at $I_e > I_c$. We classify such behavior as extrinsic length scaling.

The case when $\text{Re} z(k = 0) < 0$ and $z(k)$ rises to become positive for a given interval about some finite wave vec-

tor k_c is shown in Fig. 1(b). As the constraint I is increased to a critical value I_c, perturbations of pattern length $2\pi/k_c$ become unstable. The symmetry breaking occurs at an intrinsic pattern length determined by the kinetics and transport of the system. Note that although the linear analysis may yield one length scaling, the nonlinearities may invoke a different length scaling in the final structure.

In the sections to follow, we consider a variety of symmetry-breaking phenomena in closed systems main-
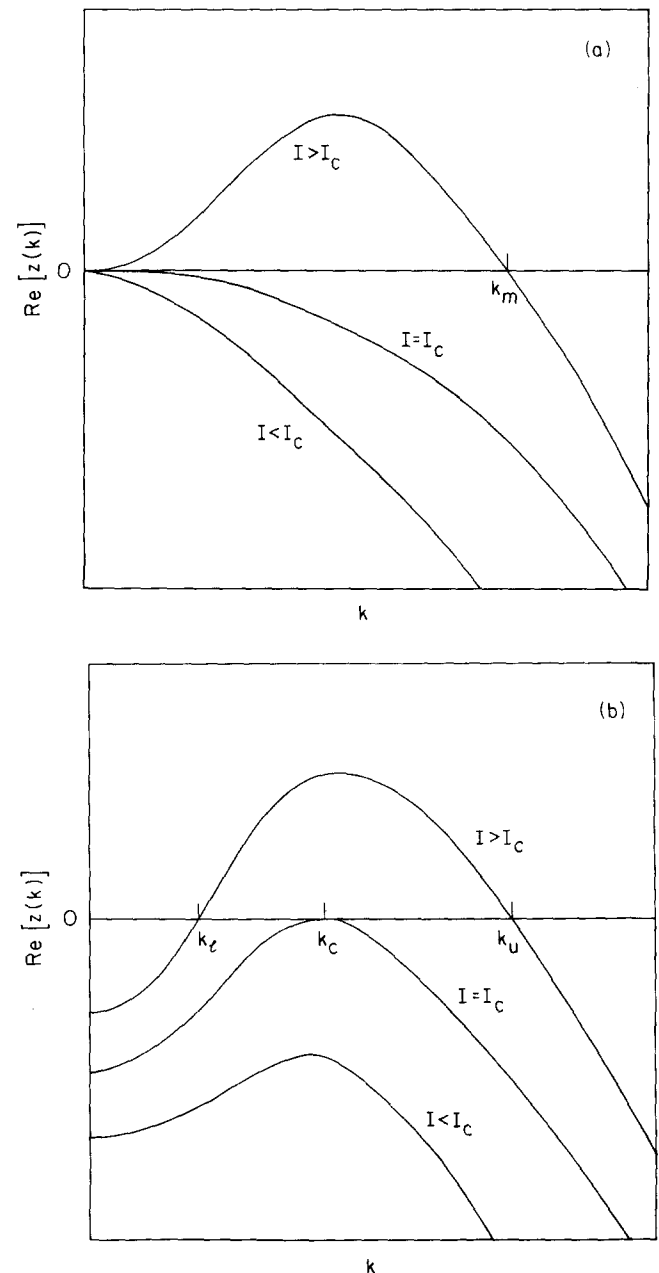

FIG. 1. Typical behavior of the real part of the stability eigenvalues $\text{Re} z$ as a function of the wave vector k. Case A is that of extrinsic length scaling, where increasing the light intensity I beyond a critical value I_c produces an interval $0 < k < k_m$ where unstable modes lie. Case B is that of intrinsic length scaling for which increasing light intensity I beyond a critical value produces an interval $0 < k_l < k < k_u$ where unstable modes lie. (See Sec. II for details.)

tained out of equilibrium by the effects of homogeneous irradiation. The analyses are made with linear stability theory, and we find examples of extrinsic and intrinsic length scaling.

III. ILLUMINATED REACTING-DIFFUSING SYSTEMS

Consider a reacting–diffusing system under isothermal and isobaric conditions and subject to homogeneous illumination. The system is closed and consists of two diffusing solute species A and B in an inert solvent. We show that such a system may undergo symmetry breaking only with extrinsic length scaling. The system is driven out of equilibrium by a photochemical process which changes the composition from the equilibrium, zero radiation, state. The nonequilibrium state is maintained by heat flow to the surroundings. The total reaction mechanism including the photochemical process(es) is described schematically by

$$A \underset{}{\overset{[I]}{\rightleftharpoons}} B , \qquad (III.1)$$

where $[I]$ indicates that photons play a role in at least one step in the reaction mechanism. Taking a matrix D of diffusion coefficients and a rate $W(A, B, I)$ for the over-all rate of the process (III.1), we obtain

$$\frac{\partial}{\partial t} \begin{bmatrix} A \\ B \end{bmatrix} = \nabla \cdot D \nabla \begin{bmatrix} A \\ B \end{bmatrix} + W(A, B, I) \begin{bmatrix} 1 \\ -1 \end{bmatrix} , \qquad (III.2)$$

where A and B are concentrations in weight per unit volume.

Since the system of volume V is closed to mass flux, we have conservation of total mass, which we express in terms of average concentrations

$$\frac{1}{V} \int d^3r \, (A + B) = \overline{C} , \qquad (III.3)$$

where $\overline{C}$ is the average total concentration of A and B. Homogeneous steady states (A_0, B_0) are determined by the condition

$$W(A_0, \overline{C} - A_0, I) = 0 . \qquad (III.4)$$

For a given real positive solution $A_0(I)$, we may consider the stability to small perturbations with dependence on space of the form e^{ikr}. The linearized equations for the perturbations $(\delta A, \delta B) = (A, B) - (A_0, B_0)$ take the general form (II.1), where the matrix $M(k)$ is given by

$$M(k) = -k^2 D + \begin{bmatrix} W_A & W_B \\ -W_A & -W_B \end{bmatrix} . \qquad (III.5)$$

Here, we define $W_A = (\partial W/\partial A)_0$ and $W_B = (\partial W/\partial B)_0$. The stability of the homogeneous steady state is found by determining the sign of the real part of the two eigenvalues $z_\pm(k)$ of $M(k)$;

$$z_\pm(k) = \tfrac{1}{2} \mathrm{Tr} M(k) \pm \tfrac{1}{2} \{ [\mathrm{Tr} M(k)]^2 - 4 \det M(k) \}^{1/2} . \qquad (III.6)$$

Thus, instability is indicated if

$$\mathrm{Tr} M(k) > 0 \qquad (III.7)$$

or

$$\det M(k) < 0 . \qquad (III.8)$$

We assume that the diffusion process is itself stable;

$$\mathrm{Tr} D > 0 , \qquad (III.9)$$

$$\det D > 0 , \qquad (III.10)$$

and that the homogeneous steady state is stable to homogeneous perturbations

$$W_A - W_B < 0 . \qquad (III.11)$$

From (III.6), we have

$$z_\pm \underset{k \to 0}{\sim} \begin{cases} W_A - W_B \\ \dfrac{k_m^2 \det D}{W_B - W_A} \, k^2 \end{cases} , \qquad (III.12)$$

where k_m will be defined in (III.14). Also, if $D_\pm$ are the eigenvalues of D, then

$$z_\pm \underset{k \to \infty}{\sim} - k^2 D_\pm . \qquad (III.13)$$

With this we see that $\mathrm{Re} z_+$ must be negative for all k. The root z_- vanishes as k^2 because homogeneous $(k = 0)$ perturbations obey the mass conservation law (III.3) that states that the homogeneous perturbations of A and B are not independent in a closed system. Since $\mathrm{Tr} M(k) < 0$, instability must arise from the condition $\det M(k) > 0$. The marginal condition $\det M(k) = 0$ is attained for the wave vector k_m if a real value of k_m is given by

$$(\det D) k_m^2 = W_A (D_{BB} + D_{AB}) - W_B (D_{AA} + D_{BA}) . \qquad (III.14)$$

Since $\det M(k)$ is quadratic in k^2, it can only vanish at most twice in k^2, and we see that we may have $z_-(k) > 0$ in an interval $0 < k < k_m$ when (III.14) yields a real value of $k_m(I)$. Hence, $z_-(k)$ takes the form shown in Fig. 1(a).

The presence of light is essential for the instability to occur. In the absence of light, the system is in thermodynamic equilibrium, and by LeChatelier's principle thus stable to all possible variations. Hence, at equilibrium, we must have $\partial W(A, B, 0)/\partial A < 0$, as addition of A must increase its rate of disappearance. Similarly, $\partial [- W(A, B, 0)]/\partial B < 0$ at equilibrium as $- W(A, B, 0)$ is the rate of formation of B. Therefore, the rhs of (III.14) is negative at equilibrium, and no real k_m exists.

We point out that simple two species model schemes may easily be constructed to demonstrate the general extrinsic symmetry-breaking phenomenon. For example,

$$P + A \rightarrow B$$

$$2A + B \rightarrow 3A$$

$$B \rightleftharpoons A \qquad (III.15)$$

may be shown to have multiple steady homogeneous states, one of which demonstrates extrinsically scaled symmetry breaking.

The analysis presented in this section proves that in a closed, two-species, illuminated, isothermal, isobaric system, only extrinsically determined symmetry breaking can occur. Thus, we are forced to go to three or more species systems in order to find intrinsically scaled symmetry breaking in such systems. Alternatively, intrinsically scaled symmetry breaking can oc-

cur in a two species nonisothermal system, as is demonstrated in the next section.

IV. INHOMOGENEOUS INSTABILITIES IN AN ILLUMINATED THERMODIFFUSIVE SYSTEM

Consider a two-component, nonreactive, gaseous system subjected to homogeneous illumination by a light that is absorbed by only one of these components. If the system is characterized by a sufficiently large thermodiffusion coefficient and if, in a thermodiffusion process, the light absorber tends to diffuse towards the higher temperature region, an instability of the homogeneous system to inhomogeneous perturbations and a spontaneous transition to an inhomogeneous distribution is expected.

Let A denote the mass density of the absorbing species. Assuming that the ideal gas equation of state is applicable, we write the hydrodynamic equations of state in the form[12]

$$\frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v} , \tag{IV.1}$$

$$\frac{dA}{dt} = -A\nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{j}_A , \tag{IV.2}$$

$$\frac{d\mathbf{v}}{dt} = -\frac{1}{\rho} \nabla \cdot P + \text{viscosity terms} , \tag{IV.3}$$

$$\frac{dT}{dt} = \frac{\theta_1}{\rho C_V} - \frac{P}{\rho C_v} \nabla \cdot \mathbf{v} - \frac{1}{\rho C_V} \nabla \cdot \mathbf{q} + \alpha A - \frac{1}{C_V} G(T, T_e)$$
$$- \frac{1}{\rho C_V} (\nabla H_A - \nabla H_B) \cdot \mathbf{j}_A - \frac{RT}{\rho C_V} \left(\frac{1}{M_A} - \frac{1}{M_B}\right) \nabla \cdot \mathbf{j}_A , \tag{IV.4}$$

where M_i is the molecular weight of component i ($i = A, B$), P the local pressure that is related to the density ρ and the temperature T through the equation of state $P = RT[A/M_A + (\rho - A)/M_B]$; $\mathbf{v}$ denotes the local center of mass velocity, A the local density of the absorber, and $\mathbf{j}_A$ the diffusion flow related to it; $\mathbf{q}$ is the heat flow, C_V is the constant volume specific heat of the system, and α is a parameter, proportional to the illumination intensity that relates the heating rate due to light absorption to the density A of the absorber (note that we assume a linear relation between the concentration A and the heating rate). Finally, θ_1 denotes the usual dissipative term [for definition see Ref. 12, Eq. (III. 38)], which is of second order in the center of mass velocity; H_i is the specific enthalpy (per unit mass) of the component i, and $G(T, T_e)$ corresponds to the local rate at which the system looses energy to the surrounding medium, which is maintained at a constant temperature T_e. The derivatives in Eqs. (IV.1)–(IV.4) are substantive derivatives

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla . \tag{IV.5}$$

In obtaining Eq. (IV.4) it is assumed that on the time scale of the experiment, heating by light absorption is instantaneous and that excited A molecules are not involved. In other words, it is assumed that the relaxation process $A^* \rightarrow A + \text{heat}$ (where A^* denotes an excited A molecule) occurs on a time scale much shorter than all the time scales involved in Eqs. (IV.1)–(IV.4). To simplify the theoretical treatment, the system is further

assumed to be bounded by an evacuated double walled long tube (Fig. 2), so that the heat loss term $G(T, T_e)$ is radiative in nature. Furthermore, we neglect boundary layer effects so that transverse gradients (perpendicular to the tube axis) are taken to be zero.

For the mass and heat flows involved in Eqs. (IV.2) and (IV.4), we assume the phenomenological relations[13] (see Appendix A)

$$-\mathbf{j}_A = L_{21} \nabla \ln T + L_{22} \frac{P}{B} \nabla \ln A , \tag{IV.6a}$$

$$-\mathbf{q} = L_{11} \nabla \ln T + L_{12} \frac{P}{B} \nabla \ln A . \tag{IV.6b}$$

These flows are subject to the boundary conditions $\mathbf{n} \cdot \mathbf{q} = \mathbf{n} \cdot \mathbf{j}_A = 0$ at the walls of the tube, where $\mathbf{n}$ is a normal to these boundary surfaces.

A homogeneous steady state with a temperature T_0 is a solution to Eqs. (IV.4, 6) provided that

$$\alpha A_0 = \frac{1}{C_V} G(T_0, T_e) . \tag{IV.7}$$

That is, the heating by radiation absorption exactly balances the radiative cooling of the system. The thermodiffusion processes of interest here occur on a time scale long relative to that required to attain hydrostatic equilibrium. Thus, since there are no external fields (i.e., gravity), the processes take place at constant pressure $\nabla P = 0$, and we may put $\mathbf{v} = 0$ and P a constant. To study the stability of this steady solution, it is sufficient to look at deviations from steady state that do not involve variations in the local center of mass velocity from its zero steady state value. (For a justification, see Appendix B.) In this case, it is sufficient to consider the reduced set of equations

$$\frac{\partial A}{\partial t} = -\nabla \cdot \mathbf{j}_A , \tag{IV.8}$$

$$\frac{\partial T}{\partial t} = -\frac{1}{\rho C_V} \nabla \cdot \mathbf{q} + \alpha A \frac{1}{C_V} G(T, T_e) - \frac{RT}{\rho C_V} \left(\frac{1}{M_A} - \frac{1}{M_B}\right) \nabla \cdot \mathbf{j}_A , \tag{IV.9}$$

where in Eq. (IV.9) we neglected terms which are of higher (≥ 2) order in deviations from homogeneity (and therefore do not contribute to the linearized equations).
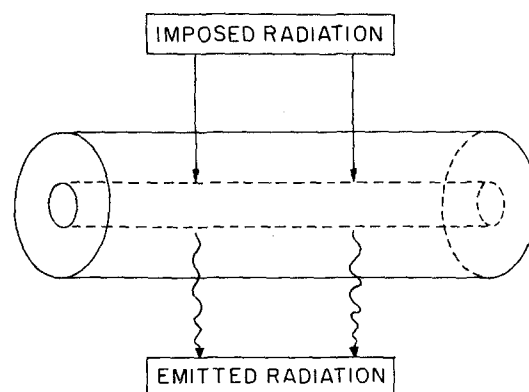

FIG. 2. Experimental configuration for tube under ambient irradiation which may be used to demonstrate symmetry-breaking instabilities in a variety of closed gaseous systems.

Linearization around the homogeneous steady state results in

$$\frac{\partial \delta A}{\partial t} = D\nabla^2 \delta A + L_1 \nabla^2 \delta T ,$$ (IV.10)

$$\frac{\partial \delta T}{\partial t} = K\nabla^2 \delta T + L_2 \nabla^2 \delta A + \alpha \delta A - \xi \delta T ,$$ (IV.11)

where

$$\xi = \frac{1}{C_V} \frac{\partial G}{\partial T} ,$$ (IV.12a)

$$D = \frac{PL_{22}}{AB} ; \qquad K = \frac{L_{11}}{\rho C_V T} + \frac{R}{\rho C_V} \left(\frac{1}{M_A} - \frac{1}{M_B} \right) L_{21} ,$$ (IV.12b)

$$L_1 = \frac{L_{21}}{T} ; \qquad L_2 = \frac{L_{12}}{\rho C_V} \frac{P}{AB} + \frac{RTP}{\rho C_V AB} \left(\frac{1}{M_A} - \frac{1}{M_B} \right) L_{22} .$$ (IV.12c)

All the quantities appearing in Eqs. (IV.10, 12) are understood to be the steady state values. Taking spatial Fourier transforms of Eqs. (IV.10, 11), we obtain, after some rearrangement,

$$\frac{\partial}{\partial t} \begin{bmatrix} \delta A \\ \delta T \end{bmatrix} = \mathbf{M} \begin{bmatrix} \delta A \\ \delta T \end{bmatrix} ,$$ (IV.13)

with

$$\mathbf{M} = \begin{bmatrix} -k^2 D & -k^2 L_1 \\ \alpha - k^2 L_2 & -(\xi + k^2 K) \end{bmatrix} .$$ (IV.14)

Since $\mathrm{Tr}\mathbf{M} < 0$, a necessary and sufficient condition for instability is

$$\det \mathbf{M} < 0 ,$$ (IV.15)

from which we deduce

$$0 < k^2 < k_m^2 \equiv -\frac{\alpha L_1 + D\xi}{KD - L_1 L_2} .$$ (IV.16)

From Eq. (IV.12), we have

$$KD - L_1 L_2 = \left(\frac{P}{AB\rho C_V T} \right)_o (L_{11} L_{22} - L_{21} L_{12}) ,$$ (IV.17)

where the subscript o indicates steady state values. The quantity on the rhs of Eq. (IV.17) is positive as the matrix of the phenomenological coefficients is positive definite. Thus, the condition (IV.16) leads to the necessary conditions

$$L_1 < 0 \text{ and } \alpha |L_1| > D\xi .$$ (IV.18)

The condition $L_1 < 0$ simply states that in the thermodiffusion process the absorber A must tend to the hotter region. The condition $\alpha |L_1| > D\xi$ is a necessary and sufficient condition for instability to occur for values of the wave vector k which are bounded by the condition (IV.16).

To study the stability properties of our system in more detail, we solve the characteristic equation $\det(\mathbf{M} - z\mathbf{I}) = 0$ by expanding z in powers of k^2. We obtain two roots which to the lowest nonvanishing order in k^2 are

$$z_1 = -\xi ,$$
$$z_2 = -(D\xi + \alpha L_1)k^2 ;$$ (IV.19)

z_2 is larger than 0 when condition (IV.18) is fulfilled. Thus, any mode of branch 2 with k^2 satisfying Eq. (IV.16) is unstable under the condition (IV.18). The dispersion curve $z_2(k)$ is of the type displayed in Fig. 1(a), where I_c is evaluated from the condition

$$\alpha(I)L_1 + D\xi = 0 .$$ (IV.20)

If the tube is of length l, the system first becomes unstable when $k_m = \pi l^{-1}$. Under these conditions the system, at least in the early stages of the development of inhomogeneity, breaks up into two regions, one rich in A and hotter and the other rich in B and cooler. This symmetry-breaking instability is obviously of the extrinsic type; its characteristic length and the threshold for its occurrence are dependent on the dimension of the system, i.e., it is a scale-variant instability.

Up to this point, the possibility of A to B conversion has been disregarded. We now show that when a reaction such as $A \rightleftharpoons B$ or $A \rightleftharpoons 2B$ is added to the kinetic scheme, the system possesses an intrinsic characteristic length. To this end, we add to the kinetic equations (IV.8–11) the chemical process

$$A \underset{W_2(A, B)}{\overset{W_1(A, B)}{\rightleftharpoons}} B$$ (IV.21)

and neglect additional couplings such as the temperature dependence of the rates W_1 and W_2. The linearized kinetic equations take the form (IV.13), where now

$$\mathbf{M} = \begin{pmatrix} -k^2 D + W & -k^2 L_1 \\ \alpha - k^2 L_2 & -(\xi + k^2 K) \end{pmatrix} ,$$ (IV.22)

in which

$$W = \left[\frac{d[W_2(A, \rho - A) - W_1(A, \rho - A)]}{dA} \right]_0 .$$ (IV.23)

The instability conditions (IV.20) are now replaced by

$$k_+^2 < k^2 < k_-^2 ,$$ (IV.24)

where

$$k_\pm^2 =$$
$$\frac{-[D\xi + \alpha L_1 - WK] \pm [(D\xi + \alpha L_1 - WK)^2 + 4W\xi(DK - L_1 L_2)]^{1/2}}{2DK - L_1 L_2}$$ (IV.25)

are those values of k^2 which satisfy the equation $\det \mathbf{M} = 0$. The dependence of the eigenvalue on the wave vector k for this system is displayed schematically in Fig. 1(b). This system is clearly characterized by an intrinsic length scale; the onset of symmetry-breaking instability corresponds to that critical intensity I_c for which $k_+^2 = k_-^2$, or, with $\alpha_c \equiv \alpha(I_c)$,

$$(D\xi + \alpha_c L_1 - WK)^2 + 4W\xi(DK - L_1 L_2) = 0 ,$$ (IV.26)

while the characteristic wave vector k_c is given by

$$k_c^2 = -\frac{D\xi + \alpha_c L_1 - WK}{2DK - L_1 L_2} .$$ (IV.27)

V. OPTICAL-ACOUSTIC INSTABILITY
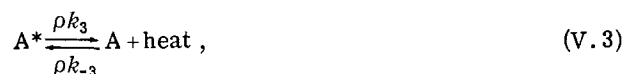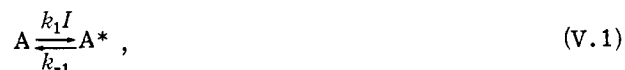
A. General

The transformation of optical energy into kinetic (thermal) energy by light absorption followed by a radiationless relaxation process has been studied mainly in relation to the measurement of vibrational relaxation rates. A well known relaxation technique of this type is the spectrophone method,[14] where a system is subjected to an amplitude modulated illumination and the resulting pressure variations are recorded by a sensitive microphone. Information on vibrational relaxation rates is then extracted from the relation of the amplitude and phase of the resulting pressure variations to those of the applied light. Another technique is provided by the impulsive optic–acoustic effect, where a single short pulse of a high intensity laser source is applied to generate a localized optically excited region within the system.[15] The consecutive radiationless relaxation processes then result in the generation of a local pressure and temperature peak (highly localized kinetic energy), which in turn give rise to the formation of sound waves. Alternatively, a modulation of the fluorescence due to the density fluctuations may be observed in both the spectrophone and the impulsive methods.[14,15]

In this section, we describe a different optical–acoustic effect; in a gaseous system, subjected to a strong homogeneous constant illumination, instability that gives rise to the spontaneous excitation of sound waves may occur. Qualitatively, this phenomenon may be described as follows; consider a one-component gas (A) homogeneously distributed in a container and subjected to a homogeneous, steady illumination by light with frequency in resonance with a convenient optical transition of the molecule A. Under steady state conditions, some of the molecules A will be in their ground state, while the remaining molecules (usually a small fraction) will be in the excited state A*. (For the sake of convenience of description, we consider a two-level case.) The radiationless relaxation A* → A is collisionally induced. This system contains a positive feedback loop. In a high density and temperature region resulting from a fluctuation or acoustic wave, the process A* → A is faster; namely, the rate of conversion of optical energy to translational kinetic energy is larger, and this leads to a further increase of the temperature in that region. This results in higher density variations in the next cycle of a spatially distributed acoustic disturbance and thus yields amplification.

For a quantitative description of this process we consider the following model.

(a) The single-component gas A is contained in a long, narrow, double-walled tube. The interspace between the two walls is evacuated so that energy exchange between the system and its surroundings occurs by blackbody radiation only. The wall of the inner tube is a perfect acoustic reflector, so that no energy is lost to the external world by work performed on the walls. The system is illuminated homogeneously (Fig. 2). This experimental situation is chosen for the sake of simplifying the theoretical treatment.

(b) The relevant reactions within the system are considered to be

$$A \underset{k_{-1}}{\overset{k_1 I}{\rightleftharpoons}} A^* ,$$ (V.1)

$$A^* \xrightarrow{k_2 I} A ,$$ (V.2)

$$A^* \underset{\rho k_{-3}}{\overset{\rho k_3}{\rightleftharpoons}} A + heat ,$$ (V.3)

where I denotes the light intensity.

The first two equations describe optical processes— absorption and (spontaneous and induced) emission. The third equation describes thermal (collisional) relaxation and excitation. The rates of these thermal processes are assumed to be proportional to the density ρ and we explicitly indicate this dependence. We introduce rate coefficients k_1' containing a factor I for the light intensity:

$$k_1' = k_1 I; \qquad k_2' = k_2 I .$$ (V.4)

(c) We assume that none of the Reactions (V.1, 2, 3) is accompanied by a volume change, and that only the heat of Reaction (V.3) is nonzero. We also assume that the system is an ideal gas.

(d) Transport coefficients are taken to be independent of the local thermodynamic state variables.

(e) Diffusion is neglected as a process of minor importance on the time scale of a few sound oscillations. Let A and A^* stand for the mass density of the species A and A*, respectively. Then we have a local conservation relation

$$A + A^* = \rho .$$ (V.5)

(f) The system is at rest at steady state (the steady state center-of-mass velocity is zero).

With these conditions the system is fully characterized by the variables ρ (local density), $\mathbf{v}$ (local center of mass velocity), X_A (local mass fraction of the component A, $X_A = A/\rho$), and the local temperature T. The time evolution is governed by the equations of irreversible thermodynamics[12]

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) ,$$ (V.6)

$$\frac{\partial \mathbf{v}}{\partial t} = -\frac{1}{\rho} \nabla p - (\mathbf{v} \cdot \nabla)\mathbf{v} + \frac{1}{\rho}\{\eta \nabla^2 \mathbf{v} + [\tfrac{1}{3}\eta + \phi]\nabla(\nabla \cdot \mathbf{v})\}$$ (V.7)

$$\frac{\partial x_A}{\partial t} = -\mathbf{v} \cdot \nabla x_A + \sum_r \nu_A^r F_r ,$$ (V.8)

$$\frac{\partial T}{\partial t} = -\mathbf{v} \cdot \nabla T - \frac{P}{\rho C_V}\nabla \cdot \mathbf{v} - \frac{1}{C_V}G(T, T_e)$$
$$+ \frac{\lambda}{\rho C_V}\nabla^2 T - \frac{1}{C_V}\sum_r \Delta H_r F_r + \frac{1}{\rho C_V}\theta_1 ,$$ (V.9)

where the notation is the same as in Sec. IV with several additions; η and ϕ are the shear and bulk viscosities. For the rth reaction ν_A^r is the stoichiometric coefficient of component A, $F_r(\rho, x_A, T)$ is the local rate of reac-

tion (see Fitts[13] and below), and ΔH_r is the enthalpy change per one gram of reaction; finally, λ is the thermal conductivity.

For simplicity, we only consider variations in the Z direction—along the tube. Thus, the viscosity terms in Eq. (V.7) may be replaced by one term of the form $(\tilde{\eta}/\rho)(\partial^2 v/\partial^2 Z)$, where $\tilde{\eta} = \frac{4}{3}\eta + \phi$. For the reactions involved we have

$$\Delta H_r = 0, \qquad r = 1, 2$$
$$\Delta H_3 = -E , \tag{V.10}$$

where $E > 0$ is the excitation energy per gram of the $A \to A^*$ transition.

For the chemical rates and the stochiometric coefficients, we have

$$\nu_A^1 = -1; \qquad F_1(x_A) = (k_1' + k_{-1}) x_A - k_{-1} ; \tag{V.11}$$

$$\nu_A^2 = 1; \qquad F_2(x_A) = -k_2' x_A + k_2'; \tag{V.12}$$

$$\nu_A^3 = 1; \qquad F_3(\rho, x_A, T) = -\rho(k_3 + k_{-3})x_A + \rho k_3 . \tag{V.13}$$

According to our assumptions, only k_3 and k_{-3} are functions of T.

The homogeneous steady state concentrations of A and A* are easily obtained. Denoting homogeneous steady state quantities by a subscript 0, we obtain

$$A_0^* = \frac{k_1 + \rho_0 k_{-3}}{k_1' + k_2' + k_{-1} + \rho_0(k_{-3} + k_3)} \rho_0 , \tag{V.14}$$

$$A_0 = \frac{k_{-1} + \rho_0 k_3 + k_2'}{k_1' + k_2' + k_{-1} + \rho_0(k_3 + k_{-3})} \rho_0 . \tag{V.15}$$

These concentrations are of course functions of the homogeneous steady state temperature which may be eliminated according to the steady state energy balance condition

$$G(T_0, T_e) = EF_2 . \tag{V.16}$$

We now inquire into the conditions for stability of the homogeneous steady states.

Linearizing the equations of motion around this homogeneous steady state and taking a spatial Fourier transform $(Z \to k)$ of all the variables, we get a set of equations in the form (II.1), $\partial \psi/\partial t = \mathbf{M}(k)\psi$, where

$$\psi = \text{col}\{\delta\rho, \delta x_A, \delta v, \delta T\} . \tag{V.17}$$

The matrix $\mathbf{M}$ is given in Appendix C, and δv represents the longitudinal (Z) component of $\delta \mathbf{v}$.

The temporal evolution of a perturbation of wave vector k may be written as a sum of terms of the form $\exp(z_n(k)t)$, where $z_n(k)$ is the nth eigenvalue of $\mathbf{M}(k)$. If $\text{Re} z_n(k)$ is positive for a given n, then the corresponding perturbations of wave vector k will grow. The behavior of the various branches (n) of the eigenvalue spectrum $z_n(k)$ in a given region of k depends on the relative time scales for sound and for thermoconductive, viscous, and chemical relaxation process in that range of wave vectors.

B. High frequency behavior

We focus our attention on cases where the relaxation processes take place on a much longer time scale than that of the sound oscillations. The square of the adiabatic sound frequency is given by

$$\omega_s^2 = \gamma P_\rho k^2 , \tag{V.18}$$

where $P_\rho = (\partial P/\partial \rho)_T$ and γ is the specific heat ratio.

In terms of this quantity, the characteristic equation $\det[\mathbf{M}(k) - Z]$, given by Eq. (C.10), may be written in the form

$$z^4 + a_3 z^3 + (a_2^2 + \omega_s^2) z^2 + (a_1^3 + b_1 \omega_s^2)z + b_0^2 \omega_s^2 = 0 , \tag{V.19}$$

where the coefficients a_i and b_i are frequencies which correspond to the time scales of reaction, viscous flow, or thermal diffusion and may be derived from the matrix $\mathbf{M}$ (see Appendix C).

An expansion procedure for this high frequency acoustic behavior is carried out by studying the limit in which ω_s is much greater than any conductive, viscous, or reactive inverse lifetime. Formally, for the conductive and viscous terms, we go to the limit of high frequency while keeping the product of the transport coefficient and the square of the wave vector constant and small relative to ω_s. Thus, we introduce the expansion

$$z \overset{\omega_s^2 \to \infty}{\sim} \sum_{n=1}^{-\infty} \zeta_n \omega_s^n \tag{V.20}$$

into the characteristic equation (V.19). In this limit, we obtain a pair of acoustic roots $z_\pm$ with imaginary part of order ω_s and real part on the slower time scale,

$$\text{Im}(z_\pm) \sim \pm \omega_s , \tag{V.21a}$$

$$\text{Re}(z_\pm) \sim \frac{1}{2}\left(M_{33} + \frac{\gamma-1}{\gamma} M_{44} + \frac{\rho_0}{\gamma T_0} M_{41}\right) . \tag{V.21b}$$

The sign of the real part of $z_\pm$ determines whether we have sound attenuation or amplification under the given conditions. In most applications, we expect k_{-3} to be very small, which is the case provided that $E \gg k_B T_0$, i.e., the optical excitation energy is much larger than the thermal energy at the steady state temperature, while k_3 is a very weak function of temperature. We also note that, assuming an Arrhenius-type temperature dependence of k_{-3}, that is

$$k_{-3} = \kappa_{-3} \exp\left(-\frac{R_{-3}}{T}\right) , \tag{V.22}$$

we get

$$\frac{\partial k_{-3}}{\partial T} = \frac{R_{-3}}{T^2} k_{-3} , \tag{V.23}$$

which is also small if k_{-3} is sufficiently small. We may thus neglect the terms involving the temperature derivatives of k_3 and k_{-3}, and using Appendix C obtain

$$M_{33} = -\tilde{\eta} k^2/\rho_0 , \tag{V.24}$$

$$M_{44} = -\xi - \frac{\lambda}{\rho_0 C_V} k^2 , \tag{V.25}$$

$$M_{41} = \frac{E}{C_V} k_3 (x_A*)_0 ; \tag{V.26}$$

or

$$\text{Re}(z_\pm) = -\tfrac{1}{2}\left[k^2\left(\frac{\bar\eta}{\rho_0}+\frac{\gamma-1}{\gamma}\frac{\lambda}{\rho_0 C_V}\right)+\frac{\gamma-1}{\gamma}\xi\right]+\frac{\rho_0}{\gamma T_0}\frac{E}{C_V}k_3(x_{A^*})_0 .$$
(V.27)

$(x_{A^*})_0 = (A^*/\rho)_0$ is given as a function of the external temperature and the illumination intensity by simultaneously solving (V.14) and (V.16).

Some comments need to be made on this development.

(a) The result (V.27) is obtained as an approximation valid in the high frequency regime. This regime is a physically interesting one, as there are many systems for which the time scale for sound oscillations may be made shorter than that for the other relaxation processes.

(b) The real part of $z_\pm(k)$, (V.27), contains a positive contribution that is proportional to the steady state fraction $(x_{A^*})_0$ of the excited A molecules. This is counterbalanced by negative contributions which correspond to the various dissipative processes: viscosity (the $\bar\eta$ term), heat conduction (the λ term), and radiative heat loss (the ξ term).

(c) Since we neglected thermal excitation by using the approximations (V.25, 26) for M_{44} and M_{41}, we have $x_{A^*} > 0$ only in the presence of illumination. For this same reason, the attenuation (negative) terms in $\text{Re}(z_\pm)$ do not contain contributions from the thermal excitation $A \to A^*$. When these approximations are not valid (for example at high steady state temperature, $T \gtrsim E/R$), then the thermal excitation process induces sound attenuation.

(d) Under conditions in which $\text{Re}(z_\pm) > 0$, spontaneous excitation of sound waves in the illuminated system may occur. Note that the range (k) of modes that may be spontaneously excited is bounded from below by the length l of the tube $2\pi/k > \tfrac{1}{2}l$, and from above by the viscous and thermal conductive dissipative terms, because these grow like k^2. In an allowed range of k, the modes that may grow are of course those which fulfill the boundary conditions, namely

$$k = \frac{n\pi}{l}, \qquad n = 0, \pm 1, \cdots .$$
(V.28)

(e) By monitoring the attenuation of sound as a function of illumination intensity until the threshold for amplification is reached, one may obtain information on the transport coefficients λ, $\bar\eta$, and ξ and on the rate coefficient k_3. In particular, the threshold condition $\text{Re}(z_\pm) = 0$ provides a valuable relation between these constants.

(f) The positive contribution to Eq. (V.27) may be recast in a different form, which makes the calculation of the condition for instability and sound amplification easier. For this, we make use of the steady state equation (V.16) which, with the neglect of k_{-3}, leads to the relation

$$\frac{1}{C_V}G(T_0, T_e) = \frac{E}{C_V}\rho_0 k_3 (x_{A^*})_0 .$$
(V.29)

Thus, the positive contribution to Eq. (V.27) is simply $(1/\gamma C_V T_0)G(T_0, T_e)$. A necessary condition for observing sound amplification may be obtained by comparing the radiative loss term to the positive term in (V.27). This corresponds to the balance of local processes and the neglect of transport terms. We obtain

$$\frac{1}{2}\frac{\gamma-1}{\gamma}\xi < \frac{1}{\gamma C_V T_0}G(T_0, T_e) .$$
(V.30)

With (A9) and the fact that $\gamma = C_P/C_V$ (> 1), we then have

$$\frac{1}{2}\left(\frac{\partial \ln G}{\partial \ln T}\right)_{T_0} < \frac{1}{\gamma-1} .$$
(V.31)

Assuming for G the relation $G = \alpha(T^4 - T_e^4)$ (as is the case for cooling by blackbody radiation), we find for (V.31) the form

$$\gamma - 1 < \frac{1}{2}\left(1 - \frac{T_e^4}{T_0^4}\right) .$$
(V.32)

The maximum value of the rhs of this inequality is $\tfrac{1}{2}$. The inequality (V.32) is never satisfied for a monatomic gas for which $\gamma = \tfrac{5}{3}$. This is, however, an uninteresting case. We expect the steady state temperature T_0 to be large enough so that at least the rotational degrees of freedom contribute to the specific heats. For a nonlinear triatomic molecule, for example, we get

$$\gamma = \frac{C_P}{C_V} < \frac{9}{7} = 1.28 ,$$
(V.33)

and the inequality (V.32) is fulfilled for

$$T_0 \gtrsim 1.21\, T_e ,$$
(V.34)

which may be achieved for sufficiently strong illumination and low external temperature. For a larger molecule with low frequency vibrations, γ is smaller and the condition is easier to fulfill.

(g) A simple representation of the quantity $\text{Re}(z_\pm)$ is also obtained if we do not neglect $\partial k_3/\partial T$, but still disregard k_{-3}. In this case, instead of (V.25), we have [according to (C8)]

$$M_{44} = -\frac{\lambda}{\rho C_V}k^2 - \xi + \frac{E}{C_V}\rho_0(x_{A^*})_0\left(\frac{\partial k_3}{\partial T}\right)_0 .$$
(V.35)

Taking for k_3 the temperature dependence conventionally attributed to vibrational relaxation rates,

$$k_3 = \kappa_3 \exp\left(-\frac{R_3}{T^{1/3}}\right) ,$$
(V.36)

we obtain

$$\frac{\partial k_3}{\partial T} = \frac{1}{3}\frac{R_3}{T^{4/3}}k_3$$
(V.37)

so that, utilizing (V.29) and Appendix C we arrive at

$$M_{44} = -\frac{\lambda}{\rho C_V}k^2 - \xi + \frac{1}{3}\frac{R_3}{T_0^{4/3}C_V}G(T_0, T_e) ,$$
(V.38)

$$M_{41} = \frac{\rho_0}{C_V}G(T_0, T_e) .$$
(V.39)

Inserting now (V.24), (V.38), and (V.39) into (V.21b), we find

$$\mathrm{Re}(z_\pm) = -\tfrac{1}{2}k^2\left(\frac{\tilde{\eta}}{\rho_0} + \frac{\gamma-1}{\gamma}\frac{\lambda}{\rho_0 C_V}\right)$$
$$-\frac{1}{2}\frac{\gamma-1}{\gamma}\xi + \frac{1}{\gamma C_V T_0}\left(\frac{(\gamma-1)R_3}{3T_0^{1/3}}+1\right)G(T_0,\,T_e)\ .$$

$$(\text{V. 40})$$

In this case, the positive contribution to $\mathrm{Re}(z_\pm)$ is greater by a factor of $1+(\gamma-1)R_3/3T_0^{1/3}$ than that obtained in neglecting the temperature dependence of k_3. The necessary condition for sound amplification (V. 32) is now replaced by a less stringent inequality:

$$\gamma - 1 < \tfrac{1}{2}\left(1 - \frac{T_e^4}{T_0^4}\right)\left(1 + \frac{(\gamma+1)R_3}{3T_0^{1/3}}\right)\ . \qquad (\text{V. 41})$$

Our stability analysis has been carried through only for the high frequency regime. A second physically interesting limit is one for which the vibration–translation relaxation rate occurs on a time scale short compared to the acoustic period.

VI. APPLICATIONS

Homogeneous steady illumination has been shown to produce a variety of nonequilibrium effects. An interesting feature of these phenomena is that they may all be attained in systems closed to mass flux. Optical energy is converted to other forms before finally being converted to and eliminated as thermal energy. The possible intermediate energy forms are chemical and mechanical (acoustic) and may also include electrical energy in appropriate illuminated electrochemical systems.

These intermediate energy forms may be used to produce systems such as motors and batteries by appropriate coupling to other systems. For example, the pressure variations in the optical–acoustic system of Sec. V may be used to drive a piston at one end of the tube at the resonance frequency. If the work done by the piston, held in rest position by a spring, is sufficiently small, then the optical–acoustic phenomena will continuously provide mechanical energy by direct conversion from electromagnetic energy.

The conditions for the onset of instability involve relations between rate and transport coefficients, external temperature, and imposed photon flux. Thus, measurements of critical illumination intensities and external and internal steady state temperature (or generally internal thermodynamic state) provides a measurement of the rate and transport coefficients. More detailed relaxation type experiments involve a pulse perturbation followed by the regression of the system back to the steady state. The functional dependence of the divergence of the relaxation lifetime at the point of marginal stability provides additional information on the rate and transport coefficients. In particular, the theory of Sec. V presents itself as a method for measuring vibration–translation relaxation rates. Unlike the spectrophone method,[14] the present one is not restricted by mechanical difficulties (upper bounds on the chopping frequency).

Closed homogeneously illuminated systems may have multiple steady states.[10] Transformations between steady states may involve large changes in temperature

and pressure. Thus, the local initiation of such transformation in a gas bears resemblance to a chemically reacting system in which detonation fronts may occur.[16]

Finally, we note that the role of light may be taken by other forms of irradiation; for instance, ambient electron flux in a discharge tube.

APPENDIX A: PHENOMENOLOGICAL RELATIONS FOR THE THERMODIFFUSIVE SYSTEM (SEC. IV)

To identify a convenient system of fluxes and forces, we begin with the expression for the entropy production, due to heat and mass flows, which is given by ϕ/T, where

$$\phi = -q\cdot\nabla\ln T - \mathbf{j}_A\cdot\nabla_T\mu_A - \mathbf{j}_B\cdot\nabla_T\mu_B\ . \qquad (\text{A1})$$

Here, $\nabla_T\mu$ is the gradient which does not include the contribution from the dependence of μ on T. As $\mathbf{j}_A = -\mathbf{j}_B$, Eq. (A1) may be recast in the form

$$\phi = -\mathbf{q}\cdot\nabla\ln T - \mathbf{j}_A\cdot\nabla_T(\mu_A - \mu_B)\ . \qquad (\text{A2})$$

We can use the coefficients of the independent fluxes q and j_A as the relevant forces and write phenomenological relations between these fluxes and forces. Utilizing further the assumption that the system is maintained in mechanical equilibrium, we have[12]

$$A\nabla_T\mu_A = -B\nabla_T\mu_B\ , \qquad (\text{A3})$$

so that the force associated with $\mathbf{j}_A$ is $(\rho/B)\nabla_T\mu_A$. With the relation $\mu_A = \mu^\circ(P,\,T)+RT\ln(A/\rho)$, and noting that ρ is a function of T only ($\rho=(RT/P)$, with P a constant at mechanical equilibrium), we get

$$\frac{\rho}{B}\nabla_T\mu_A = \frac{\rho RT}{B}\nabla\ln A = \frac{P}{B}\nabla\ln A\ , \qquad (\text{A4})$$

which in turn leads directly to the phenomenological relations, Eq. (IV. 6).

APPENDIX B

We outline the conditions for which we can disregard Eqs. (IV. 1) and (IV. 3) and consider only the reduced set (IV. 8, 9) in the stability analysis of the thermodiffusive system (Sec. IV). The physical basis for this approximation is that sound energy is absorbed (or lost into the surrounding) on a time scale much shorter than other characteristic times in the system. For simplicity, we take the case of overdamped sound, where the damping is shorter than the period of the acoustic period at wave vectors of interest. The attainment of hydrostatic equilibrium through transmission of sound through the walls is usually treated phenomenologically in standard acoustics texts. Here, we shall represent it also by adding a term $-(1/\tau)\mathbf{v}$ to the velocity equations. Our assumption is then that $\kappa=1/\tau$ is much larger in magnitude than any other term in the coefficient matrix of the linearized equations of motion. This set of equations is of the form

$$\frac{d}{dt}\begin{bmatrix} v \\ \rho \\ A \\ T \end{bmatrix} = \begin{bmatrix} -\kappa & a_{12} & a_{13} & a_{14} \\ a_{21} & 0 & 0 & 0 \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{bmatrix}\begin{bmatrix} v \\ \rho \\ A \\ T \end{bmatrix} . \qquad \text{(B1)}$$

It is evident that for our purpose it is sufficient to use the theorem: For the matrix $\mathbf{A} = (a_{ij})$, let $a_{11} \equiv -\kappa$. When $\kappa \to \infty$, there is one root which equals $-\kappa$ (to leading order in κ), while the rest of the eigenvalues are of order 1 and are given to this order by the eigenvalues of the matrix that is obtained from $\mathbf{A}$ by eliminating the first row and column.

The proof is straightforward. The characteristic equation $|\mathbf{A} - \omega\mathbf{I}| = 0$ is solved by an expansion of the form

$$\omega = \sum_{n=1}^{-\infty} \omega_n \kappa^n . \qquad \text{(B2)}$$

Taking the matrix $\mathbf{A}$ to be $N \times N$, we obtain to order κ

$$(-\omega_1)^N - (\omega_1)^{N-1} = 0 \qquad \text{(B3)}$$

yielding $\omega_1 = -1, 0, 0, \cdots, 0$. For the $N-1$ roots for which $\omega_1 = 0$, the highest order term in the expansion of the characteristic equation is of order 1, and we find that ω_0 is given by the eigenvalues of the matrix

$$\begin{bmatrix} a_{22} & \cdots & a_{2N} \\ \vdots & & \vdots \\ \vdots & & \vdots \\ a_{N2} & \cdots & a_{NN} \end{bmatrix} ,$$

thus completing the proof.

APPENDIX C

We present here some of the intermediate formulae involved in the stability analysis of the optical acoustic system studied in Sec. V. For simplicity of notation, we drop the subscript zero which denotes the steady state value.

The stability matrix $\mathbf{M}(k)$ takes the form

$$\mathbf{M}(k) = \begin{bmatrix} 0 & 0 & -ik\rho & 0 \\ M_{21} & M_{22} & 0 & M_{24} \\ -ikP_\rho/\rho & 0 & M_{33} & ikP_T/\rho \\ M_{41} & M_{42} & -ikP/\rho C_V & M_{44} \end{bmatrix} , \qquad \text{(C1)}$$

in which $P_\rho = (\partial P/\partial \rho)_{T,x_A}$ and $P_T = (\partial P/\partial T)_{\rho,x_A}$. The matrix elements M_{ij} in (C1) are given by

$$M_{21} = k_3 x_{A*} - k_{-3} x_A , \qquad \text{(C2)}$$

$$M_{22} = -[k_1' + k_{-1} + k_2' + \rho(k_3 + k_{-3})] , \qquad \text{(C3)}$$

$$M_{24} = \rho\left[x_{A*}\left(\frac{\partial k_3}{\partial T}\right) - x_A\left(\frac{\partial k_{-3}}{\partial T}\right)\right] , \qquad \text{(C4)}$$

$$M_{33} = -\bar{\eta}k^2/\rho_0 , \qquad \text{(C5)}$$

$$M_{41} = EM_{21}/C_V , \qquad \text{(C6)}$$

$$M_{42} = -E(k_3 + k_{-3})\rho/C_V , \qquad \text{(C7)}$$

$$M_{44} = -\lambda k^2/\rho C_V - \xi + \frac{E}{C_V}M_{24} . \qquad \text{(C8)}$$

We define the linear coefficient ξ for the radiative heat loss as

$$\xi = \frac{1}{C_V}\left(\frac{\partial G}{\partial T}\right)_0 . \qquad \text{(C9)}$$

The characteristic equation $\det[\mathbf{M} - z] = 0$ then takes the form

$$z^4 - \mathrm{Tr}\,\mathbf{M}z^3 + [M_{22}M_{23} + M_{22}M_{44} + M_{33}M_{44} - M_{24}M_{42} + \gamma P_\rho k^2]z$$
$$- [M_{22}M_{33}M_{44} - M_{24}M_{33}M_{42} + k^2(\gamma P_\rho M_{22} + P_\rho M_{44} - P_T M_{41})]z$$
$$+ \Delta = 0 ,$$

where $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (C10)

$$\Delta = -k^2 \det\begin{bmatrix} M_{21} & M_{22} & M_{24} \\ P_\rho & 0 & P_T \\ M_{41} & M_{42} & M_{44} \end{bmatrix} . \qquad \text{(C11)}$$

For an ideal gas, $P_T = P/T$ and $P_\rho = P/\rho$.

Note added in proof. After submission of this manuscript we learned of the work of H.-J. Bauer and H. E. Bass [Phys. Fluids 16, 988 (1973)] in which they study amplification of sound by radiation (the topic considered in Sec. V).

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