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Light Scattering from Systems with Chemical Oscillations and Dissipative Structures*

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The spectrum of light scattered from a system of coupled nonlinear chemical reactions is considered for steady states far from equilibrium. Fluctuations from a steady state may exhibit oscillatory decay, marginally stable chemical oscillations, or dissipative structures. Qualitatively new features appear in the spectrum when compared to the light scattering spectrum from reacting systems at equilibrium. The principal new features found are splittings in the chemical lines and dispersive (non-Lorentzian) contributions. Two model reaction mechanisms, the Volterra–Lotka model and the Prigogine–Lefever model, are examined in detail.

I. INTRODUCTION

Far from equilibrium coupled nonlinear reaction schemes may have steady state compositions which are stable or marginally stable.[1,2] If the steady state is stable then fluctuations in composition will regress back to that state but may do so with oscillations. If the steady state compositions are marginally stable then composition fluctuations of a particular wavelength will be undamped. In unstable systems fluctuations grow with time, either in an oscillatory or monotonic manner. Far from chemical equilibrium coupled reactions may also be in stable limit cycles: Concentrations of species vary periodically and fluctuations decay to the stable limit cycle.[3] Since the light scattering spectrum is directly proportional to the Fourier transform of composition fluctuations we expect that such systems will give qualitatively new features in the spectrum. The purpose of this paper is to investigate the new features that may be encountered in light scattering from chemically reacting systems far from equilibrium. The scattering of light from systems with hydrodynamic instabilities (Bénard problem) has been studied.[4,5]

Our intent is to explore the possible use of light scattering to study these systems and the calculations we present on model systems should be considered suggestive. For some references on related experiments see Refs. 3 and 6–8.

For chemical systems at equilibrium the spectrum of light scattered from the composition fluctuations leads to superimposed Lorentzians centered at zero frequency $\omega=0$.[9–11] The reason for this is that the matrix describing the linear regression of concentration fluctuations is real and can be made symmetric. Hence, the eigenvalues of the matrix are all real and the associated modes (eigenvectors) exhibit simple exponential decay in time. For systems far from chemical equilibrium, the matrix describing the linear regression of fluctuations need not be symmetric. Hence, the modes may exhibit oscillatory decay if their associated eigenvalues are complex. Such an oscillatory mode will appear in the spectrum as a doublet with intensity symmetrically placed at $\pm\omega_c$, where ω_c is the frequency of oscillation of the chemical mode. In addition there are non-Lorentzian contributions to the spectrum.

It appears that the spectrum of light scattered from a system far from equilibrium is richer in structure than the spectrum scattered when the system is at equilibrium. This additional structure contains useful information, for example the splittings are related to chemical rate coefficients. Since splittings are easy to measure, it is possible that it will prove easier to measure rate coefficients by light scattering in systems far from equilibrium than in systems at complete equilibrium. In the latter case it is necessary to analyze superimposed Lorentzians in the limit of forward scattering to determine a rate coefficient.

In Sec. II a simple theory is presented for light scattering from chemically reacting fluids far from equilibrium. Diffusion is the only transport mechanism taken into account other than chemical reaction. Thus the theory applies to the central or Rayleigh part of the spectrum. To extend the theory to the Brillouin doublet pressure fluctuations must be included.[12] In addition temperature variations will increase the possibilities for instability and introduce other effects not considered here. In Sec. IV two specific model reaction schemes are employed to illustrate some of the qualitative features to be expected in the spectrum.

II. LIGHT SCATTERING THEORY

The light scattered from a reacting fluid mixture is proportional to the space–time Fourier transform of the local dielectric constant autocorrelation function

$$I(\mathbf{k},\omega)=\mathrm{Re}\int_0^\infty \exp(-i\omega t)\langle\delta\epsilon^F(\mathbf{k},t)\delta\epsilon^F(-\mathbf{k})\rangle\,dt, \qquad (2.1)$$

where ω is the change in frequency on scattering and $\mathbf{k}$ is the scattering wave vector which is related to the scattering angle θ and the incident wave vector $\mathbf{k}_0$ by

$$|\mathbf{k}|=2|\mathbf{k}_0|\sin\theta/2. \qquad (2.2)$$

In Eq. (2.1) $\delta\epsilon^F(\mathbf{k},t)$ is the space Fourier transform of the local dielectric constant $\delta\epsilon(\mathbf{r},t)$. The physical assumptions underlying the expression (2.1) for the light scattering spectrum are that the dielectric constant is local in space and varies in time due to fluctuations in the fluid. The temporal fluctuations in the dielectric constant are assumed to be characterized by a stochastic process which is stationary and Gaussian.[13]

We further assume that ϵ is an implicit function of position and time through its dependence on the local thermodynamic variables. Hence, at constant temperature and pressure the fluctuations in the local dielectric constant are related to the local composition fluctuations $\delta\psi_i(\mathbf{r}, t)$ from the steady state (denoted by superscript zero) by

$$\delta\epsilon(\mathbf{r}, t) = \sum_i (\partial\epsilon/\partial\psi_i)^0{}_{T,p}\delta\psi_i(\mathbf{r}, t), \tag{2.3}$$

where the sum extends over the various species i. The intensity of the scattered light may then be expressed as

$$I(\mathbf{k}, \omega) = \text{Re}\mathbf{B}^T\cdot\int_0^\infty \exp(-i\omega t) \times\langle\delta\boldsymbol{\psi}^F(\mathbf{k}, t)\delta\boldsymbol{\psi}^F(-\mathbf{k})\rangle dt\cdot\mathbf{B}, \tag{2.4}$$

in which $\boldsymbol{\psi}^F$ is the Fourier transform of the column vector of the concentrations, $\mathbf{B}$ is a vector with ith component equal to $(\partial\epsilon/\partial\psi_i)^0{}_{T,p}$ and $\mathbf{B}^T$ is the transpose of $\mathbf{B}$.

At constant T and p the concentrations of the chemical species obey the equations

$$\partial\boldsymbol{\psi}/\partial t = \mathsf{D}\nabla^2\boldsymbol{\psi}(\mathbf{r}, t) + \mathbf{F}[\boldsymbol{\psi}], \tag{2.5}$$

where D is a matrix of diffusion coefficients and $\mathbf{F}(\boldsymbol{\psi})$ a source term due to chemical reactions, which in general obey nonlinear rate laws. We consider light scattering from fluctuations away from a spatially homogeneous steady state $\boldsymbol{\psi}^0$, and assume that the fluctuations regress to the steady state according to the macroscopic hydrodynamic equations (2.5). For small perturbations $\delta\boldsymbol{\psi} = \boldsymbol{\psi} - \boldsymbol{\psi}^0$ we obtain the linearized equations[14,15]

$$\partial\delta\boldsymbol{\psi}(\mathbf{r}, t)/\partial t = \mathsf{D}\nabla^2\delta\boldsymbol{\psi}(\mathbf{r}, t) + \boldsymbol{\Omega}(\boldsymbol{\psi}^0)\delta\boldsymbol{\psi}(\mathbf{r}, t), \tag{2.6}$$

where we have used the fact that $\mathbf{F}(\boldsymbol{\psi}^0) = 0$ for the homogeneous steady state and we have defined

$$\boldsymbol{\Omega}(\boldsymbol{\psi}^0) = (\partial\mathbf{F}/\partial\boldsymbol{\psi})_{\psi=\psi^0}. \tag{2.7}$$

The spatial Fourier transform of Eq. (2.6) is

$$\begin{aligned}\partial\delta\boldsymbol{\psi}^F(\mathbf{k}, t)/\partial t &= [-\mathsf{D}k^2 + \boldsymbol{\Omega}(\boldsymbol{\psi}^0)]\delta\boldsymbol{\psi}^F(\mathbf{k}, t)\\ &\equiv \mathsf{M}(k)\delta\boldsymbol{\psi}^F(\mathbf{k}, t)\end{aligned} \tag{2.8}$$

with the formal solution

$$\delta\boldsymbol{\psi}^F(\mathbf{k}, t) = \exp[\mathsf{M}(k)t]\delta\boldsymbol{\psi}^F(\mathbf{k}). \tag{2.9}$$

When this result is used in Eq. (2.4) and the one sided Fourier transform in time is executed, we obtain

$$I(\mathbf{k}, \omega) = \text{Re}\mathbf{B}^T\cdot[i\omega\mathsf{I} - \mathsf{M}(k)]^{-1}\cdot\langle\delta\boldsymbol{\psi}^F(\mathbf{k})\delta\boldsymbol{\psi}^F(-\mathbf{k})\rangle\cdot\mathbf{B}. \tag{2.10}$$

We formally display the spectrum by expanding respectively the vectors $\mathbf{B}^T$ and $\langle\delta\boldsymbol{\psi}^F(\mathbf{k})\delta\boldsymbol{\psi}^F(-\mathbf{k})\rangle\cdot\mathbf{B}$ in terms of an assumed complete normalized biorthogonal set of left (row) $\mathbf{Y}_n{}^L(k)$ and right (column) $\mathbf{Y}_n{}^R(k)$ eigenvectors of the matrix $\mathsf{M}(k)$,

$$\mathsf{M}(k)\cdot\mathbf{Y}_n{}^R(k) = z_n(k)\mathbf{Y}_n{}^R(k) \tag{2.11}$$

and

$$\mathbf{Y}_n{}^L(k)\cdot\mathsf{M}(k) = z_n(k)\mathbf{Y}_n{}^L(k). \tag{2.12}$$

The result is

$$I(\mathbf{k}, \omega) = \text{Re}\sum_n A_n(k)\{1/[i\omega - z_n(k)]\}C_n(k), \tag{2.13}$$

where

$$A_n(k) = \mathbf{B}^T\cdot\mathbf{Y}_n{}^R(k) \tag{2.14}$$

and

$$C_n(k) = \mathbf{Y}_n{}^L(k)\cdot\langle\delta\boldsymbol{\psi}^F(\mathbf{k})\delta\boldsymbol{\psi}^F(-\mathbf{k})\rangle\cdot\mathbf{B}. \tag{2.15}$$

The case of light scattering from a chemically reacting system at steady state differs from that at complete equilibrium by the fact that the eigenvalues (and eigenvectors) are, in general, complex. If we write the eigenvalues

$$z_n(k) = \Gamma_n(k) + i\Omega_n(k), \tag{2.16}$$

the spectrum becomes

$$\begin{aligned}I(\mathbf{k}, \omega) = \sum_n (&I_n(k)\{\Gamma_n(k)/[\omega - \Omega_n(k)]^2 + \Gamma_n(k)^2\}\\ &+ \{D_n(k)[\omega - \Omega_n(k)]/[\omega - \Omega_n(k)]^2 + \Gamma_n(k)^2\}),\end{aligned} \tag{2.17}$$

where the amplitude of the absorptive (Lorentzian) part of the spectrum $I_n(k)$ is given by

$$I_n(k) = \text{Re}[A_n(k)C_n(k)] \tag{2.18}$$

and the amplitude of the dispersive (non-Lorentzian) part of the spectrum $D_n(k)$ is given by

$$D_n(k) = I_n[A_n(k)C_n(k)]. \tag{2.19}$$

In the conventional case of light scattering from an equilibrium state[9-11] the eigenvalues and eigenvectors are real so that the spectrum becomes

$$I(\mathbf{k}, \omega) = \sum_n \{I_n(k)\Gamma_n(k)/[\omega^2 + \Gamma_n(k)^2]\}, \tag{2.20}$$

which consists of superimposed Lorentzians centered at $\omega = 0$; there is no dispersive contribution. Normally the analysis of spectra which consist of superimposed Lorentzians is most difficult. In contrast the spectrum from the steady state system, Eq. (2.19), consists of Lorentzians (distorted by dispersive contributions) centered at various frequencies $\Omega_n(\mathbf{k})$ that are in general non-zero. Provided that these frequencies are not all identical and that $\Omega_n > \Gamma_n$ the spectrum will be split into well resolved contributions. Consequently light scattering from chemically reacting systems at a steady state, where fluctuations decay with oscillations, may prove to be a better procedure for measuring fast rate coefficients than light scattering from chemically reacting systems at equilibrium.

III. TWO EXAMPLES

In this section we illustrate the structure of the spectra that may be encountered when light is scattered from a chemical system at a steady state where fluctuations decay with oscillation. The examples are not comprehensive, they have been selected to display, as simply as possible, some of the features which arise. We restrict attention here to steady states $\boldsymbol{\psi}^0$ that are either stable or marginally stable with respect to spatially homogeneous and inhomogeneous perturbations. A system is stable (or marginally stable) to homogeneous perturbations if $\text{Re}[z_n(0)]<0$ {or $\text{Re}[z_n(0)]=0$ for at least one value of n}. A system is stable (or marginally stable) to inhomogeneous perturbations if $\text{Re}[z_n(k)]<0$ for all $k\neq 0$ {or $\text{Re}[z_n(k)]=0$ for at least one $\mathbf{k}$}. This restriction assures that the fluctuations around the steady state do not grow so that the steady state $\boldsymbol{\psi}^0$ is physically attainable.

A. The Volterra–Lotka Mechanism

The Volterra–Lotka mechanism in the absence of backreactions[1,2] is

$$\mathrm{A}+\mathrm{X}\xrightarrow{k_1}2\mathrm{X},$$

$$\mathrm{X}+\mathrm{Y}\xrightarrow{k_2}2\mathrm{Y},$$

$$\mathrm{Y}\xrightarrow{k_3}\mathrm{E}. \tag{3.1}$$

We assume that species A, E, and any solvent present are optically inactive and that the concentration of A is kept constant; only fluctuations in X and Y are considered. The homogeneous steady state $\boldsymbol{\psi}^0$ is easily found to be

$$\boldsymbol{\psi}^0=\begin{pmatrix}\mathrm{X}^0\\ \mathrm{Y}^0\end{pmatrix}=\begin{bmatrix}(k_3/k_2)\\ (k_1\mathbf{A}/k_2)\end{bmatrix}. \tag{3.2}$$

The linearized equations of motion for the fluctuations $\delta\boldsymbol{\psi}=(\delta\mathbf{X},\delta\mathbf{Y})$ around this steady state satisfy Eq. (2.8) with

$$\mathsf{M}(k)=\begin{pmatrix}-D_{\mathrm{X}}k^2 & -k_2\mathbf{X}^0\\ k_2\mathbf{Y}^0 & -D_{\mathrm{Y}}k^2\end{pmatrix}, \tag{3.3}$$

where for simplicity we have assumed a diagonal matrix of diffusion coefficients. The eigenvalues of this matrix are

$$z_\pm(k)=-\tfrac{1}{2}(D_{\mathrm{X}}+D_{\mathrm{Y}})k^2\pm[(D_{\mathrm{X}}-D_{\mathrm{Y}})k^4-4k_1k_3\mathbf{A}]^{1/2}, \tag{3.4}$$

from which one may conclude that the steady state for this system is marginally stable to homogeneous perturbations and stable to inhomogeneous perturbations.

For the case of equal and diagonal diffusion coefficients we note the general result for any reaction mechanism, $z_n(k)=z_n(0)-Dk^2$, and hence for the present case we have

$$z_\pm(k)=-Dk^2\pm i(k_1k_3\mathbf{A})^{1/2}, \tag{3.5}$$

which according to Eq. (2.17) will give rise to a doublet spectrum located at

$$\pm\omega_c=\pm(k_1k_3\mathbf{A})^{1/2}. \tag{3.6}$$

Note that the splitting $2\omega_c$ is proportional to a particular factor of rate coefficients. The width of each line is (Dk^2) so that if $2\omega_c>Dk^2$ the doublet will be resolved. At the present state of the experiments in light scattering such resolution is achievable for reactions with $\omega_c>20$ Hz. As forward scattering is approached $\mathbf{k}\rightarrow 0$, and there is a progressive sharpening of the lines until at $\mathbf{k}=0$ each component is infinitely sharp for a system which is marginally stable to homogeneous perturbations.

In this example the chemical lines become infinitely sharp as $\mathbf{k}\rightarrow 0$. This is a result of the Volterra–Lotka model without back reactions. If back reactions are included, this model is stable to homogeneous perturbations and the chemical lines have finite widths at $\mathbf{k}=0$. However, the narrowing of a chemical line will be a general feature of the spectrum as a point of marginal stability is approached.

In order to display the spectrum for this case, it is necessary to compute the factors $(\partial\epsilon/\partial\psi_i)^0{}_{T,p}$ and the matrix of fluctuations at this steady state. To our knowledge there is no rigorous theory for either one of these quantities. For illustrative purposes we shall make the assumptions

$$(\partial\epsilon/\partial\mathrm{X})^0{}_{T,p}=(\partial\epsilon/\partial\mathrm{Y})^0{}_{T,p}=\alpha_p \tag{3.7}$$

and

$$\langle\delta\psi_i{}^F\delta\psi_j{}^F\rangle=\beta_i\delta_{ij}\qquad i,j=\mathrm{X},\mathrm{Y}. \tag{3.8}$$

It should be emphasized that the calculation of the spectrum can be accomplished for choices of these quantities other than (3.7) and (3.8). Two points about these approximations should be noted. First, the assumption of equal effective polarizabilities α_p for each species, in the case of light scattering from chemically reactive fluids at equilibrium, leads to no contribution of the chemical process to the spectrum. Second, a great deal of literature exists on different procedures for computing the matrix $\langle\delta\boldsymbol{\psi}\delta\boldsymbol{\psi}\rangle$.[3,16] A particularly intriguing suggestion[15] is that some elements of this fluctuation matrix behave anomalously as a point of marginal stability is approached. Such anomalous behavior will be manifested in the spectrum.

With the assumptions Eqs. (3.7)–(3.8), the spectrum may easily be calculated. The result is

$$[I(\mathbf{k},\omega)/\alpha_p{}^2]$$

$$=(\beta_X+\beta_Y)\left[\frac{\Gamma(k)}{(\omega+\omega_c)^2+\Gamma(k)^2}+\frac{\Gamma(k)}{(\omega-\omega_c)^2+\Gamma(k)^2}\right]$$

$$+\Lambda(k)\left[\frac{(\omega-\omega_c)}{(\omega-\omega_c)^2+\Gamma(k)^2}-\frac{(\omega+\omega_c)}{(\omega+\omega_c)^2+\Gamma(k)^2}\right], \quad (3.9)$$

where the chemical frequency ω_c is given by Eq. (3.6), the width $\Gamma(k)$ by $\Gamma(k)=Dk^2$, and

$$\Lambda(k)=\tfrac{1}{2}[(\beta_Y\mathbf{X}^0-\beta_X\mathbf{Y}^0)/(\mathbf{X}^0\mathbf{Y}^0)^{1/2}]; \quad (3.10)$$

the contribution of the dispersive term may be important.

A similar analysis can be carried out for the case where $D_X\neq D_Y$. The essential difference is that the eigenvalues are not necessarily complex for all values of **k** and hence a splitting of the chemical lines will not be present at all angles. From Eq. (3.4) we can see that $z_\pm(k)$ has a complex part only if

$$k<(4k_1k_3\mathbf{A}/|D_X-D_Y|)^{1/4}\equiv k_c \quad (3.11)$$

so that a splitting will only appear for angles such that $k<k_c$.

B. The Prigogine–Lefever Mechanism[17]

As a second example we consider the model reaction scheme which has received some attention[2,3,17–19]

$$\mathrm{A}\xrightarrow{k_1}\mathrm{X},$$

$$2\mathrm{X}+\mathrm{Y}\xrightarrow{k_2}3\mathrm{X},$$

$$\mathrm{B}+\mathrm{X}\xrightarrow{k_3}\mathrm{Y}+\mathrm{D},$$

$$\mathrm{X}\xrightarrow{k_4}\mathrm{E}. \quad (3.12)$$

Here again we consider only fluctuations in **X** and **Y**; the species A, B, E are assumed to be optically inactive and present at fixed concentrations. Furthermore for ease of analysis we shall consider only the special case where all the rate coefficients are equal to a single value κ and $\mathrm{A}=1$, $\mathrm{B}=b$. Under these circumstances, the steady state concentrations are $\mathbf{X}^0=1$, $\mathbf{Y}^0=b$. If we assume a diagonal matrix of diffusion constants the matrix $\mathsf{M}(k)$ appearing in the linearized equation of motion for the fluctuations $\delta\psi=(\delta\mathbf{X},\delta\mathbf{Y})$ is

$$\mathsf{M}(k)=\begin{bmatrix}-D_Xk^2+(b-1)\kappa & \kappa\\ -b\kappa & -D_Yk^2-\kappa\end{bmatrix}. \quad (3.13)$$

The eigenvalues of this matrix are

$$z_\pm(k)=-\tfrac{1}{2}\{[D_Xk^2+D_Yk^2+(2-b)\kappa]\pm[f(k^2,b)]^{1/2}\}, \quad (3.14)$$

where

$$f(k^2,b)=\gamma_0(b)+\gamma_1(b)k^2+\gamma_2k^4 \quad (3.15)$$

with

$$\gamma_0(b)=(2-b)^2\kappa^2-4\kappa^2,$$

$$\gamma_1(b)=2b(D_Y-D_X)\kappa,$$

$$\gamma_2=(D_X-D_Y)^2. \quad (3.16)$$

At $\mathbf{k}=0$ the eigenvalues are

$$z_\pm(0,b)=-\tfrac{1}{2}[(2-b)\kappa\pm(\gamma_0)^{1/2}]. \quad (3.17)$$

From this we may conclude that the steady state is stable to homogeneous perturbations for $b<2$ and marginally stable for $b=2$.

The situation with regard to inhomogeneous perturbations is more complicated. The result will depend on the ratio of the diffusion constants (D_X/D_Y), which we denote α. For fixed α and b we must see if there is a real, positive value of k^2 at which the real part of the largest root $z_-(k^2,b)$ vanishes. This condition implies the existence of a real, positive value of k^2 given by the expression

$$k_\pm{}^2=(\kappa/2D_X)\{(b-1-\alpha)\pm[(b-1-\alpha)^2-4\alpha]^{1/2}\}. \quad (3.18)$$

Analysis of this discriminant shows that, provided

$$b<[1+(\alpha)^{1/2}]^2\equiv b_c, \quad (3.19)$$

no real value of k^2 will exist that makes z_- vanish. Thus when $b<b_c$ the system is stable to inhomogeneous perturbations; at $b=b_c$ the system becomes marginally stable to inhomogeneous perturbations. We may conclude that according to the value of α there are two regions of interest. If $0<\alpha<(3-2\sqrt{2})$ then $b_c<2$ and b must be less than b_c to assure stability with respect to inhomogeneous perturbations. If $\alpha>(3-2\sqrt{2})$ then $b_c>2$ and b must be less than 2 to assure stability with respect to homogeneous perturbations. We consider several possible cases in turn.

1. *Case* (1): $\alpha=1$

For this case of equal diffusion coefficients the condition for stability requires that $b<2$; the two eigenvalues are

$$z_\pm(k,b)=-\{Dk^2+[1-(b/2)]\kappa\}\pm i\omega_c, \quad (3.20)$$

where

$$\omega_c=[-\gamma_0(b)]^{1/2}=\kappa\{1-[1-(b/2)]^2\}^{1/2} \quad (3.21)$$

and we have taken into account that $\gamma_0<0$ for $b<2$. The spectrum may easily be computed for this case and we find with the assumptions Eqs. (3.7)–(3.8), a shape identical to Eq. (3.9) with the width given by

$$\Gamma(k)=Dk^2+[1-(b/2)]\kappa, \qquad (3.22)$$

the chemical frequency ω_c by Eq. (3.21), and

$$\Lambda(k)=(\kappa/2\omega_c)[(b/2)(\beta_X+\beta_Y)-\beta_Y]. \qquad (3.23)$$

The width ω_c is a monotonically increasing function of b, reaching a maximum value at $b=2$ where $\omega_c=k$. At small b where ω_c is small the quantity $\Lambda(k)$, which measures the amplitude of the dispersive part of the spectrum, becomes large.

As $b\rightarrow 2$ the system approaches marginal stability. The quantities which characterize the spectrum approach the values

$$\Gamma(k)\rightarrow Dk^2, \qquad \omega_c\rightarrow\kappa, \qquad \Lambda(k)\rightarrow\beta_X/2. \qquad (3.24)$$

The widths are completely determined by diffusion and the doublet lines sharpen as $\mathbf{k}\rightarrow 0$. The separation of the doublet components $2\omega_c$ is independent of $\mathbf{k}$.

2. *Case* (2): $\alpha\neq 1$, $\alpha>(3-2\sqrt{2})$

For this case of unequal diffusion coefficients the stability condition requires $b<2$ and the eigenvalues are given by Eq. (3.14). We examine the behavior of $f(k^2, b)$ in Eq. (3.15). This function may be written for $b<2$ as

$$f(k^2, b)=-|\gamma_0|+|\gamma_1|k^2+|\gamma_2|k^4 \qquad 1\geq\alpha>(3-2\sqrt{2}),$$

$$f(k^2, b)=-|\gamma_0|-|\gamma_1|k^2+|\gamma_2|k^4 \qquad \alpha\geq 1 \qquad (3.25)$$

with $\gamma_1=\gamma_2=0$ at $\alpha=1$.

If $f(k^2, b)$ is negative $z_\pm(k, b)$ becomes complex and the spectrum is split by an amount

$$2\omega_c=2[-f(k^2, b)]^{1/2}. \qquad (3.26)$$

The width $\Gamma(k)$ when $f(k^2, b)<0$ is

$$\Gamma(k)=\tfrac{1}{2}[D_Xk^2+D_Yk^2+(2-b)\kappa]. \qquad (3.27)$$

If $f(k^2, b)$ is positive, $z_\pm(k, b)$ is real and negative and the spectrum is not split.

Consideration of Eq. (3.25) shows that for $1>\alpha>(3-2\sqrt{2})$ the splitting is largest at $\mathbf{k}=0$ and decreases until it vanishes at

$$k_L=\{[\alpha/(1-\alpha)](\kappa/D_X)[2(b)^{1/2}-b]\}^{1/2}. \qquad (3.28)$$

If the scattering angle is such that $\mathbf{k}>\mathbf{k}_L$ there is no splitting.

For $\alpha>1$ the splitting first increases and then decreases as $\mathbf{k}$ is increased from $\mathbf{k}=0$. The splitting vanishes at

$$k_U=\{[\alpha/(\alpha-1)](\kappa/D_X)[b+2(b)^{1/2}]\}^{1/2}, \qquad (3.29)$$

and if the scattering angle is such that $k>k_U$ there is no splitting. The special value $\alpha=1$ has been treated above. The behavior of the spectrum as the system approaches marginal stability may easily be determined.

3. *Case* (3): $0<\alpha<(3-2\sqrt{2})$

For this case of unequal diffusion with $D_Y\gg D_X$ the stability condition requires $b\leq b_c$, where b_c is given by Eq. (3.19). The analysis of this case for $b\leq b_c$ closely follows Case (2). For example the splitting in the spectrum vanishes at values of k_L given by Eq. (3.28).

It is particularly interesting to examine the behavior of the spectrum as a function of angle at the point $b=b_c$ where the system becomes marginally stable to inhomogeneous perturbations. According to Eq. (3.18) for this value of b the eigenvalue $z_-(k, b)$ will be zero at $k_+^2=[\kappa\alpha/D_X]$. Since for this value of b, $k_L^2=\kappa\alpha/D_X<k_+^2$, there is no splitting and $z_-(k, b)$ is real in the neighborhood of k_+. When $z_-=0$ we expect an infinitely sharp line at zero frequency. The behavior of $z_-(k, b_c)$ as a function of k^2 in the neighborhood of k_+^2 will determine the width of this component in the neighborhood of the critical angle defined by k_+^2. A simple calculation yields

$$z_-(k, b_c)=-(\kappa/\alpha)[(1-\alpha)(1+\alpha^{-1/2})]^{-1} \times(D_X/\kappa)^2(k^2-k_+^2)^2. \qquad (3.30)$$

Since $z_-<0$ except at k_+^2 we may conclude that at marginal stability $(b=b_c)$ the fluctuations with wave vectors infinitesimally larger or smaller than the critical wave vector k_+ will be stable. This fact will be manifest in the light scattering spectrum at marginal stability by small but symmetric widths as a function of k^2 about k_+^2 for the sharp component of the spectrum. This feature may serve as an experimental diagnostic of a marginal stable state.

IV. CONCLUDING REMARKS

The spectrum of scattered light exhibits the time dependence of the regression of fluctuations (through the dielectric constant) and hence provides information about the eigenvalues of the fluctuations. The spectrum is predicted to contain qualitatively different features when the system is in a steady state far from equilibrium compared to that for a system at complete equilibrium. We have considered some simple examples to illustrate this point. Generalizations are possible in a number of directions; for instance other features may be expected in the spectrum when the effects of nondiagonal diffusion coefficients are considered. Furthermore we have restricted the discussion to fluctuations from stable (time-independent) steady states. The study of fluctuations from a time-dependent homogeneous state, the time dependence being due to either relaxation or a stable limit cycle, requires further analysis, both with respect to the fundamental equation of light scattering, Eq. (2.1), and the calculation of concentration fluctuations around nonstationary states. In addition we have limited ourselves to isobaric and isothermal fluctuations. Instabilities involving reactions and temperature fluctuations are common in chemical engineering applications. For example, phenomena such as singing flames[20] exemplify instabilities involving the interaction of reaction, temperature and pressure fluctuations. Destabilization of acoustic modes in reacting fluids has been studied.[12,21,22]

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[1] P. Glansdorff and I. Prigogine, *Thermodynamic Theory: Structure, Stability, and Fluctuations* (Wiley, New York, 1971).

[2] J. Higgins, Ind. Eng. Chem. **59**, 18 (1967).

[3] G. Nicolis, Advan. Chem. Phys. **19**, 209 (1971).

[4] V. M. Zaitsev and M. I. Shliomis, Zh. Eksp. Teor. Fiz. **59**, 1583 (1970) [Sov. Phys. JETP **32**, 866 (1971)].

[5] Jean-Pierre Boone, "Spectral Analysis of a Fluid under Thermal Constraint," J. Stat. Phys. (to be published).

[6] R. M. Noyes, R. J. Field, E. Körös, J. Am. Chem. Soc. **94**, 1394 (1972).

[7] H. Degn, J. Chem. Ednc. **49**, 302 (1972).

[8] A. T. Winfree, Science **175**, 634 (1972).

[9] B. J. Berne and H. L. Frisch, J. Chem. Phys. **47**, 3675 (1967).

[10] B. J. Berne, J. M. Deutch, J. T. Hynes, and H. L. Frisch, J. Chem. Phys. **49**, 2864 (1968).

[11] L. Blum and Z. W. Salsburg, J. Chem. Phys. **50**, 1654 (1969) and references cited therein.

[12] R. G. Gilbert, H. Hahn, P. J. Ortoleva, and J. Ross, J. Chem. Phys. **57**, 2672 (1972).

[13] See for example L. D. Landau and E. M. Litfshitz, *Electrodynamics of Continuous Media* (Pergamon, London, 1960), Chaps. XIII, XIV.

[14] M. Lax, Rev. Mod. Phys. **32**, 25 (1960).

[15] R. M. Mazo, J. Chem. Phys. **52**, 3306 (1970).

[16] G. Nicolis and A. Babloyantz, J. Chem. Phys. **51**, 2632 (1969).

[17] I. Prigogine and P. Lefever, J. Chem. Phys. **48**, 1695 (1968).

[18] A. M. Turing, Phil. Trans. Roy. Soc. (London) **B237**, 37 (1952).

[19] P. J. Ortoleva and J. Ross, J. Chem. Phys. **55**, 4378 (1971); **56**, 287, 293, 4397 (1972).

[20] G. M. Markstein, *Non-Steady Flame Propagation* (MacMillan, New York, 1964).

[21] T. Y. Toong, Combust. Flame, **18**, 207 (1972).

[22] R. G. Gilbert, P. J. Ortoleva, and J. Ross (unpublished).

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Simplified Multiconfiguration Self-Consistent-Field Theory for Localized Orbitals. I Fixed Orbitals*

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We develop a simplified version of the fixed orbital multiconfiguration self-consistent-field theory (MC–SCF–FXO) for localized orbitals of Gilbert by analyzing the operators and matrix elements in powers of the overlap, neglecting terms quadratic and higher in overlap. This procedure eliminates many terms found in the complete theory. The matrix elements of the orbital operators are particularly simple since all strictly environmental terms and many of the subsystem–environment interaction terms vanish. The orbital and secular equations are then decomposed into equations for a subsystem coupled to its environment. A scheme for the self-consistent solution of these equations is discussed.

I. INTRODUCTION

The main purpose of this paper is to develop a simplified version of fixed orbital multiconfiguration self-consistent-field theory (MC–SCF–FXO) for use in large polyatomic systems. Our starting point is the exact MC–SCF–FXO theory recently derived by Gilbert.[1] In Sec. II we briefly summarize the principal results of this theory and obtain the multiconfiguration generalization of the Adams–Gilbert equation[2] for localized orbitals. In Sec. III we analyze the operators appearing in the MC–SCF theory. We first decompose these operators into r-body parts making use of the Jacobi expansions of the second and third order normalized density and transition operators; then we obtain the decomposition of the MC operators into "atomic," intra-atomic overlap, and interatomic overlap parts; next we analyze the MC operators in powers of the overlap and neglect terms which are quadratic and higher in overlap; finally we analyze the matrix elements of the orbital operators in powers of the overlap neglecting all terms quadratic and higher in overlap. In Sec. IV we decompose the orbital and secular equations into equations for a subsystem coupled to its environment, making use of the operator analysis of the previous section, and present a scheme for the solution of these equations.

II. FIXED ORBITAL MULTICONFIGURATION THEORY

We briefly summarize the principal results of the multiconfiguration self-consistent-field theory recently derived by Gilbert.[1] The wavefunction for the polyatomic system is chosen to be the sum of N Slater determinants each constructed from a subset $[\phi_{i_1}\cdots\phi_{i_n}]$ of a common set[3,4] $[\phi_1\cdots\phi_m]$ of fixed orbitals, as follows:

$$\Psi=\sum C_I\Phi^I, \qquad (1)$$

where

$$\Phi^I=(n!)^{-1/2}\,||\,\phi_{i_\mu}(x_\nu)\,|| \qquad \mu,\nu=1,n. \qquad (1')$$