On the significance of finite propagation speeds in multicomponent reacting systems

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A continuum model of diffusion in a reacting mixture is built around a constitutive relation for momentum exchange by frictional interaction between diffusing species. The resulting continuity and momentum equations incorporate a finite relaxation time for diffusion. Under appropriate conditions, linearization of these equations produces a coupled system of hyperbolic equations for small disturbances of a stationary state. Fick's law can be recovered from the linear equations by assuming instantaneous relaxation of the flux, provided that the stationary state is uniform. Fick's law is generally inconsistent with the momentum equation when the stationary state is nonuniform. The stability of uniform stationary solutions predicted by the parabolic system obtained when Fick's law is used is compared with the stability predicted by the hyperbolic system. When the former predicts stability and has at least one pair of complex-conjugate roots, the latter may predict that the stationary state is unstable. Thus, inclusion of relaxation in the model can lead to qualitatively different predictions of stability.

I. INTRODUCTION

In the majority of experiments on diffusion in systems slightly perturbed from a steady state, a "Fick's-law" type of linear constitutive relation between the diffusive flux of a species and gradients of the field variables is adequate to correlate observations. However, it is widely recognized that this constitutive relation, and its counterpart in heat conduction, Fourier's law, are strictly valid only for describing steady-state phenomena.[1] Use of Fick's law for transient diffusion leads to a parabolic partial differential equation, and such equations predict that density disturbances can travel at arbitrarily large velocities. Such predictions are physically meaningless, and to obviate this difficulty alternate constitutive equations must be sought.

From a molecular viewpoint, the reasons for the meaningless predictions derived by using Fick's law are evident. Einstein showed[2] that for Brownian particles the relationship $\langle r^2\rangle \propto t$, between the mean square displacement and the time elapsed since their release, is only asymptotically valid for large t. The complete relation is

$$\langle r^2\rangle = \frac{2mkT}{f^2}\left[\frac{ft}{m} - 1 + e^{-ft/m}\right],$$

where m is the mass and f the friction coefficient of a particle and kT is the unit of molecular energy. At large times this reduces to $\langle r^2\rangle \propto t$, but when $t \ll m/f$, then $\langle r^2\rangle \sim (kT/m)^2 t^2$. The latter relation shows that during a short time interval following release of the particles, the average motion is wavelike. In the transition region between these extremes, the motion relaxes from the wavelike $\langle r^2\rangle \propto t^2$ to the random, diffusionlike $\langle r^2\rangle \propto t$, and any equation that governs the motion of an ensemble of Brownian particles must have a solution with similar properties. One such equation, often suggested as an alternate to the diffusion equation, is a damped wave equation called the telegrapher's equation. Goldstein[3] showed that it is the governing equation for a random walk in which successive steps are correlated.

Although interdiffusion of approximately equally-sized particles differs from the Brownian motion model of a massive particle subject to randomly fluctuating forces, the qualitative features of the two processes are undoubtedly similar. The ensemble motion of a group of molecules released at a point is highly correlated, hence wavelike, during some short interval following their release, but gradually relaxes, as the correlations decay owing to interactions with other molecules, to a random, diffusive motion. An estimate of the relaxation time (10^{-10}–10^{-11} sec) suggests that there will be no significant qualitative difference between a description of diffusion based on Fick's law and one that incorporates a finite relaxation time. This has been shown rigorously for a nonreacting ideal binary mixture,[4] but it has not been established for any single-component system with a nonlinear reaction or for a linearized description of a multicomponent reacting mixture. Turing[5] and others[6] have shown that open multicomponent systems can be unstable as a result of interactions between reaction and diffusion, even when the two processes would be stable were each to occur separately. Here we investigate whether the relaxation effect is always negligible in linearized multicomponent reacting systems, and if it is not, under what circumstances its inclusion leads to qualitatively different predictions of stability.

In any continuum model of reaction and diffusion, the conservation equations must be supplemented by constitutive equations that relate reaction rates, rates of transport, stresses, etc. to the field variables. In Sec. II, we follow recent work in the continuum theory of mixtures[7] and postulate constitutive relations for the reaction rates and for the rate of exchange of linear momentum between species due to "frictional" interactions. The individual species momentum balance equations then yield a system of partial differential equations for the diffusion fluxes. Postulating the relation for frictional interaction between species has the advantage that the relaxation of the flux is automatically accounted for by the momentum equation; no *ad hoc* assumption of rate-type constitutive equations for the fluxes is required.

When linearized, the conservation equations lead to a coupled system of partial differential equations for density and flux disturbances. Linearization around a non-

uniform, nonequilibrium steady state produces equations in which the flux disturbance depends on the steady-state value of the flux, as well as on the steady-state densities and their perturbations. Even when relaxation effects are ignored, Fick's law is not recovered. Only when the steady state is uniform can one recover Fick's law. Because the linear equations have nonconstant coefficients if the steady state is nonuniform, we treat only uniform steady states in Sec. III. The general solution of the initial-boundary value problem is derived and compared with the solution obtained using Fick's law.

The inclusion of the finite relaxation time has two major effects. First, it introduces n new dynamical modes for the time evolution of the amplitudes in a Fourier expansion of the solution. Generally these modes are rapidly damped, and hence insignificant, except for a very short time interval following a disturbance. Secondly, it rotates a certain subspace of the $2n$ dimensional "amplitude" space and perturbs the eigenvalues of the n slowly-decaying modes. Whether these eigenvalues are perturbed sufficiently to alter the qualitative time behavior of the n slow modes is studied in Sec. IV.

II. EQUATIONS OF CHANGE FOR DENSITIES AND FLUXES

The system is an $n+1$-component reacting mixture contained in the region $0 \le x \le L$, $0 \le y \le L$, $0 \le z \le \delta$ of three space, and surrounded by a uniform, constant-composition bath. Both system and surroundings are isothermal and characterized by a single temperature. Mass exchange between system and surroundings can occur only across the planes $z=0$ and $z=\delta$; the remainder of the boundary is closed. For simplicity we assume that $\delta/L \ll 1$ and that composition nonuniformities are negligible in the z direction. The upcoming equations for densities and fluxes, which depend only on x and y, may be regarded as averages of their three-dimensional version over the z dimension.[8] For convenience we work in mass densities rather than molar densities and we assume that there are $n+1$ chemical species, of which the $n+1$st neither reacts nor is transferred across the boundary.

Let ρ_i, $\mathbf{v}^i$, and $\mathbf{j}^i$ denote the density, velocity, and diffusion flux of species i in the system; the latter defined as $\mathbf{j}^i \equiv \rho_i(\mathbf{v}^i - \mathbf{v})$, where $\mathbf{v} \equiv \sum_i \rho_i \mathbf{v}^i / \sum_i \rho_i$ is the mass average velocity relative to fixed coordinates. Further, let R_i be the mass rate of production of i; N_i the rate of exchange of i with the surroundings; $\mathbf{T}^i$ the stress tensor of species i; and $\mathbf{F}^i$ the net rate at which linear momentum is supplied to species i. The balance equations for mass and momentum are

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \rho_i \mathbf{v} = -\nabla \cdot \mathbf{j}^i + R_i + N_i ,$$
$$\frac{\partial}{\partial t}(\rho_i \mathbf{v}^i) + \nabla \cdot \rho_i \mathbf{v}^i \mathbf{v}^i = \nabla \cdot \mathbf{T}^i + \mathbf{F}^i . \tag{1}$$

By summing these equations over i, one obtains the over-all equations for total density ρ and total momentum $\rho\mathbf{v}$:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = N,$$
$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot \rho \mathbf{v}\mathbf{v} = \nabla \cdot \mathbf{T} + \mathbf{F} . \tag{2}$$

Here $\rho \equiv \sum_i \rho_i$, $N \equiv \sum_i N_i$, $\mathbf{F} \equiv \sum_i \mathbf{F}^i$, and $\mathbf{T} \equiv \sum_i [\mathbf{T}^i - \rho_i(\mathbf{v}^i - \mathbf{v}) \times (\mathbf{v}^i - \mathbf{v})]$ are the total density, total mass exchange rate, total momentum supply rate, and total stress tensor, respectively, of the mixture.

The momentum supply rates $\mathbf{F}^i$ consist of four terms,

$$\mathbf{F}^i = \mathbf{F}^i_d + \mathbf{F}^i_r + \mathbf{F}^i_e + \mathbf{F}^i_b . \tag{3}$$

As written, they represent the net rate of increase of linear momentum of species i due to frictional interaction with all other species, to chemical reaction, to mass exchange with the surroundings, and to the action of conservative external fields. Because the internal interactions between species have no effect on the total linear momentum, it is necessary[9] that both

$$\sum \mathbf{F}^i_d = 0$$

and

$$\sum_i \mathbf{F}^i_r = 0 . \tag{4}$$

The body force and exchange terms will be neglected hereafter.

For later purposes it is more convenient to regard $(\rho_1, \cdots \rho_{n+1}, \mathbf{j}^1, \cdots \mathbf{j}^{n+1})$ as the dependent variables rather than $(\rho_1, \cdots, \rho_{n+1}, \mathbf{v}^1, \cdots, \mathbf{v}^{n+1})$. The two sets are related by a nonsingular transformation, and either can be recovered from the other. In terms of the $\mathbf{j}^i$'s, the species momentum equations at (1) read

$$\frac{\partial \mathbf{j}^i}{\partial t} + \nabla \cdot \frac{\mathbf{j}^i \mathbf{j}^i}{\rho_i} + \frac{\rho_i}{\rho}[\nabla \cdot \mathbf{T} + \mathbf{F} - \mathbf{v}N] + \nabla \cdot \mathbf{v}\mathbf{j}^i + \mathbf{v}\nabla \cdot \mathbf{j}^i + \nabla \cdot \mathbf{j}^i \mathbf{v} + \nabla \cdot (\rho_i - \rho)\mathbf{v}\mathbf{v} = \nabla \cdot \mathbf{T}^i + \mathbf{F}^i , \tag{5}$$

and after rearrangement the over-all momentum equation reads

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = \nabla \cdot \mathbf{T} + \mathbf{F} - \mathbf{v}N . \tag{6}$$

Equations (1a), (2a), (5), and (6), when augmented by boundary conditions and constitutive equations for the reaction rates, exchange rates, viscous stresses, and momentum supplies, suffice to determine the density and diffusive fluxes of all species.[10]

The constitutive equations cannot be arbitrarily chosen because they must reflect the symmetry of the material to which they apply and must be invariant under orthogonal transformations of space time.[11] We assume that the reacting mixture is isotropic and find that a set of constitutive equations consistent with the foregoing restrictions is

$$
\begin{aligned}
&R_i = R_i(\rho_1, \ldots, \rho_n) \\
&N_i = N_i(\rho_1, \ldots, \rho_n, \rho_1^0, \ldots, \rho_n^0)
\end{aligned}
\Big\} i = 1, \ldots, n
$$

$$
\begin{aligned}
\mathbf{F}_d^i &= \mathbf{F}_d^i(\rho_1, \ldots, \rho_{n+1}, \mathbf{j}^1, \ldots, \mathbf{j}^{n+1}) \\
&= \sum_{k=1}^{n} \phi_k^i(\rho_1, \ldots, \rho_{n+1}, |\mathbf{j}^1|, \ldots, |\mathbf{j}^{n+1}|, \\
&\quad \mathbf{j}^1 \cdot \mathbf{j}^2, \ldots, \mathbf{j}^{n-1} \cdot \mathbf{j}^n)\mathbf{j}^k \qquad (7) \\
\mathbf{F}_r^i &= \mathbf{F}_r^i(\rho_1, \ldots, \rho_{n+1}, \mathbf{j}^1, \ldots, \mathbf{j}^{n+1}) \\
&= \sum_{k=1}^{n} \psi_k^i(\rho_1, \ldots, \rho_{n+1}, |\mathbf{j}^1|, \ldots, |\mathbf{j}^{n+1}|, \\
&\quad \mathbf{j}^1 \cdot \mathbf{j}^2, \mathbf{j}^{n-1} \cdot \mathbf{j}^n)\mathbf{j}^k \\
\mathbf{T}^i &= -p^i(\rho_1, \ldots, \rho_n)\underline{\delta}
\end{aligned}
$$

where all functions are smooth functions of their arguments.[12] Here $\rho_1^0, \ldots, \rho_n^0$ are the densities in the surroundings; p^i is the hydrostatic pressure of species i; $|\ |$ is the magnitude of a vector in 2-space; $\cdot$ is the scaler product of vectors in 2-space; and $\underline{\delta}$ is the unit isotropic second rank tensor.

The postulated stress relationship reflects the assumption that each constituent of the mixture behaves as a perfect fluid and implies that the total stress is given by $\mathbf{T} = -p\underline{\delta} - \sum_i (1/\rho_i)\mathbf{j}^i\mathbf{j}^i$. The functions ϕ_k^i and ψ_k^i are isotropic, scalar-valued functions and depend, as indicated, only on the scalar invariants of the set $\{\mathbf{j}^1, \ldots, \mathbf{j}^{n+1}\}$.[13] Clearly both $\mathbf{F}_d^i$ and $\mathbf{F}_r^i$ vanish when all fluxes vanish, but it must also be true that for nonzero fluxes $\sum_i \mathbf{F}_d^i = \sum_i \mathbf{F}_r^i = \mathbf{0}$; this implies that the ϕ_k^i and ψ_k^i must satisfy $\sum_i \phi_k^i = \sum_i \psi_k^i = 0$. Furthermore, the momentum supply $\mathbf{F}_r^i$ must vanish when $R_i = 0$ and this further restricts the ψ_k^i. When the Jacobian $[\partial R_i/\partial \rho_i]$ is nonsingular for all ρ_j in the range of interest, (7a) can be inverted to give $\rho_j = \rho_j(R_1, \ldots, R_n)$ and (7d) can then be written as $\mathbf{F}_r^i = \sum \psi_k^i(R_1, \ldots, R_n, |\mathbf{j}^1|, \ldots, |\mathbf{j}^{n-1} \cdot \mathbf{j}^n)\mathbf{j}^k$, where the ψ_k^i are now different functions. They must satisfy $\sum_i \psi_k^i = 0$ and $\psi_k^i(R_1, \ldots 0, \ldots R_n, |\mathbf{j}^1|, \ldots \mathbf{j}^{n-1} \cdot \mathbf{j}^n) = 0$.

A complete analysis of the full nonlinear problem given by (1a), (2a), (5), and (6) with initial and boundary conditions is impossible, even if linear reaction mechanisms are under consideration. Accordingly, we restrict attention to the behavior of the solution in the neighborhood of a steady state and study the linearization of the nonlinear equations. We assume that the system of steady-state equations, obtained by setting $(\partial/\partial t) = 0$ in (1a), (2a), (5), and (6), has at least one solution $(\tilde{\rho}_1, \ldots \tilde{\rho}_{n+1}, \tilde{\mathbf{j}}^1, \ldots, \tilde{\mathbf{j}}^{n+1}, \tilde{\mathbf{v}})$ for which $\tilde{\mathbf{v}} = \mathbf{0}$, $\tilde{\rho}_k \geq 0$, and at least one $R_i \neq 0$. Such a solution satisfies

$$
\begin{aligned}
&-\nabla \cdot \tilde{\mathbf{j}}^i + R_i + N_i = 0, \\
&N = 0, \\
&\nabla \cdot \frac{\tilde{\mathbf{j}}^i\tilde{\mathbf{j}}^i}{\rho_i} = -\nabla\tilde{p}^i + \tilde{\mathbf{F}}_d^i + \tilde{\mathbf{F}}_r^i - \nabla\tilde{p} \qquad (8) \\
&\qquad -\nabla \cdot \sum_i \tilde{\rho}_i\tilde{\mathbf{j}}^i\tilde{\mathbf{j}}^i + \sum \mathbf{F}_r^i = 0, \\
&\tilde{\mathbf{j}}^i = \mathbf{0} \text{ on the boundary,}
\end{aligned}
$$

where a tilde denotes a quantity evaluated at the steady state. Define $\hat{\rho}_i$, $\hat{\mathbf{j}}^i$, and $\hat{\mathbf{v}}$ as disturbances of such a steady state and set $\mathbf{j} \equiv (\hat{\mathbf{j}}^1, \ldots, \hat{\mathbf{j}}^{n+1})^T$, $\rho \equiv (\hat{\rho}_1, \ldots, \hat{\rho}_{n+1})^T$. To first order, the disturbances satisfy the linear equations

$$
\begin{aligned}
&\frac{\partial\rho}{\partial t} + \nabla \cdot \mathbf{j} - K\rho = 0, \\
&\frac{\partial\mathbf{j}}{\partial t} + \underline{\Omega}_1 \cdot \nabla\mathbf{j} + \underline{\Omega}_1(\nabla \cdot \mathbf{j}) + \underline{\Omega}_2 \cdot \mathbf{j} + \Omega_3\mathbf{j} + \underline{\Omega}_4 \cdot \nabla\rho + \Omega_5\nabla\rho + \underline{\Omega}_6\rho + \underline{\Omega}_7 \cdot \hat{\mathbf{v}} + \tilde{\mathbf{j}}(\nabla \cdot \hat{\mathbf{v}}) + \tilde{\mathbf{j}} \cdot \nabla\hat{\mathbf{v}} + (\nabla \cdot \mathbf{j})\hat{\mathbf{v}} = 0, \\
&\frac{\partial\hat{\rho}}{\partial t} + \nabla \cdot \tilde{\rho}\hat{\mathbf{v}} = \sum_{j,k} \frac{\partial N_j}{\partial \rho_k}\hat{\rho}_k, \qquad (9) \\
&\tilde{\rho}\frac{\partial\hat{\mathbf{v}}}{\partial t} = -\nabla\hat{p} - \sum_k \left[\nabla \cdot \left(\frac{\tilde{\mathbf{j}}^k\hat{\mathbf{j}}^k + \hat{\mathbf{j}}^k\tilde{\mathbf{j}}^k}{\tilde{\rho}_k}\right) - \nabla \cdot \left(\frac{\hat{\rho}_k\tilde{\mathbf{j}}^k\tilde{\mathbf{j}}^k}{\tilde{\rho}_k^2}\right)\right] + \sum_{i,k} \tilde{\psi}_i^k\hat{\mathbf{j}}^k + \sum_{i,j,k} \frac{\partial\psi^i}{\partial R_j}\frac{\partial R_j}{\partial \rho_k}\tilde{\mathbf{j}}^i\hat{\rho}_k,
\end{aligned}
$$

where the constants are defined as

$$
\begin{aligned}
(\underline{\Omega}_1)_{ik} &= \frac{\mathbf{j}^k}{\rho_k}\delta_{ik} - \frac{\tilde{\rho}_i\tilde{\mathbf{j}}^k}{\tilde{\rho}\tilde{\rho}_k}, \\
(\underline{\Omega}_2)_{ik} &= \left[\nabla\frac{(\tilde{\mathbf{j}}^k)}{\tilde{\rho}_k}\right]^T\delta_{ik} - \frac{\tilde{\rho}_i}{\tilde{\rho}}\left[\nabla\frac{(\tilde{\mathbf{j}}^k)}{\tilde{\rho}_k}\right]^T \\
&\quad - \sum_q \sum_{p \geq q} \frac{\partial(\phi_k^i + \psi_k^i)}{\partial(\mathbf{j}^p \cdot \mathbf{j}^q)}\tilde{\mathbf{j}}^k\tilde{\mathbf{j}}^p, \\
(\Omega_3)_{ik} &= \nabla \cdot (\tilde{\mathbf{j}}^k/\tilde{\rho}_i)\delta_{ik} - \frac{\tilde{\rho}_i}{\tilde{\rho}}\nabla \cdot (\tilde{j}^k/\tilde{\rho}_k) - (\tilde{\phi}_k^i + \tilde{\psi}_k^i), \\
(\underline{\Omega}_4)_{ik} &= -\frac{\tilde{\mathbf{j}}^k\tilde{\mathbf{j}}^i}{\tilde{\rho}_i^2}\delta_{ik} + \frac{\tilde{\mathbf{j}}^k\tilde{\mathbf{j}}^k}{\tilde{\rho}_k^2}, \\
(\Omega_5)_{ik} &= \sum_q \left(\delta_{iq} - \frac{\tilde{\rho}_i}{\tilde{\rho}}\right)\frac{\partial p^q}{\partial \rho_k},
\end{aligned}
$$

$$
\begin{aligned}
(\underline{\Omega}_6)_{ik} &= \left[-\tilde{\mathbf{j}}^k\frac{(\nabla \cdot \tilde{\mathbf{j}}^i)}{\tilde{\rho}_i^2} - \tilde{\mathbf{j}}^k \cdot \nabla(\tilde{\mathbf{j}}^k/\tilde{\rho}_k^2)\right]\delta_{ik} + \tilde{\mathbf{j}}^k\nabla(\tilde{\mathbf{j}}^k/\tilde{\rho}_k^2) \\
&\quad + \tilde{\mathbf{j}}^k\frac{(\nabla \cdot \tilde{\mathbf{j}}^k)}{\tilde{\rho}_k^2} - \sum_q \frac{\partial\phi_q^i}{\partial\rho_k}\tilde{\mathbf{j}}^k - \sum \frac{\partial\psi^i}{\partial R_q}\frac{\partial R_q}{\partial\rho_k}\tilde{\mathbf{j}}^k, \qquad (10) \\
(\underline{\Omega}_7)_i &= 2[\nabla\tilde{\mathbf{j}}^i]^T, \\
K_{ij} &= \frac{\partial R_i}{\partial\rho_j} + \frac{\partial N_i}{\partial\rho_j}, \\
\delta_{ij} &= \text{Kronecker delta.}
\end{aligned}
$$

Only $2(n+1)$ of the disturbance variables are independent and these are most conveniently taken as $\hat{\rho}_1, \ldots, \hat{\rho}_{n+1}$, $\hat{\mathbf{v}}$, $\hat{\mathbf{j}}^1, \ldots, \hat{\mathbf{j}}^n$. From these follow $\hat{\rho} = \sum_{k=1}^{n+1}\hat{\rho}_k$, $\hat{\mathbf{j}}^{n+1} = -\sum_{k=1}^{n}\hat{\mathbf{j}}^k$, and $\hat{p} = \sum_{k=1}^{n+1}\hat{p}_k = \sum_{j,k=1}^{n+1}(\partial p^k/\partial\rho_j)\hat{\rho}_j$.

The linearized momentum equation in (9) gives the most general linear relation between the flux, density, velocity, and their space and time derivatives that is consistent with the postulated constitutive equations. Since both space and time derivatives of the flux appear in the equation, it is clear that one cannot generally recover a Fick's law relation simply by ignoring the time derivative of $\mathbf{j}$ and the velocity terms. Therefore, Fick's law will generally be inconsistent with the linearized species momentum equations, even when the small departures from a steady state are time independent and such that $\hat{\mathbf{v}} = \mathbf{0}$. It is interesting to note that spatial "relaxation" of the flux, as reflected by the terms involving spatial derivatives, appears automatically and on an equal footing with temporal relaxation in this derivation.

In the foregoing case, the coefficients in (9) depend on the stationary state and therefore (9) cannot be solved in general. Consequently, we shall hereafter assume that the stationary state is uniform, in which case the flux equations reduce substantially. Now both $\nabla \cdot \tilde{\mathbf{j}}^i = 0$ and $\nabla \wedge \tilde{\mathbf{j}}^i = 0$, and since $\tilde{\mathbf{j}}^i = 0$ on the boundary, $\tilde{\mathbf{j}}^i \equiv 0$, i.e., all fluxes vanish identically. As a result, the constants $\underset{\sim}{\Omega}_1$, $\underset{\sim}{\Omega}_2$, $\underset{\sim}{\Omega}_4$, $\underset{\sim}{\Omega}_6$, and $\underset{\sim}{\Omega}_7$ all reduce to zero, and

$$
\begin{aligned}
(\Omega_3)_{ik} &= -(\tilde{\phi}^i_k + \tilde{\psi}^i_k) \equiv \Phi_{ik}\,, \\
(\Omega_5)_{ik} &= \sum \left(\delta_{iq} - \frac{\tilde{\rho}_i}{\tilde{\rho}}\right) \frac{\partial p^q}{\partial \rho_k} \equiv C_{ik}\,.
\end{aligned}
\tag{11}
$$

The equations at (9) now reduce to

$$
\begin{aligned}
&\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} - K\rho = 0, \\
&\frac{\partial \mathbf{j}}{\partial t} + \Phi \mathbf{j} + C \nabla \rho = \mathbf{0}\,, \\
&\tilde{\rho} \frac{\partial \hat{\mathbf{v}}}{\partial t} = -\nabla \hat{p} + \sum_{i,k} \tilde{\psi}^k_i \hat{\mathbf{j}}^k
\end{aligned}
\tag{12}
$$

with initial and boundary conditions

$$
\begin{aligned}
&\rho(x, y, 0) = \rho_0(x, y), \\
&\mathbf{j}(x, y, 0) = \mathbf{j}_0(x, y), \\
&\hat{\mathbf{v}}(x, y, 0) = \hat{\mathbf{v}}_0(x, y), \\
&\mathbf{j}(0, y, t) = \mathbf{j}(L, y, t) = \mathbf{j}(x, 0, t) = \mathbf{j}(x, L, t) = \mathbf{0}
\end{aligned}
\tag{13}
$$

for $0 \le x \le L$, $0 \le y \le L$, $t \ge 0$. The ρ and $\mathbf{j}$ equations of (12) are not coupled to the $\hat{\mathbf{v}}$ equation and can be solved independently. Knowing ρ and $\mathbf{j}$, $\hat{\mathbf{v}}$ follows from

$$
\hat{\mathbf{v}}(x, y, t) = \mathbf{v}(x, y, 0) - \sum_{k,q} \int_0^t \left[\frac{\partial p^k}{\partial \rho_q} \hat{\rho}_q(x, y, \tau) - \delta_{kq} \tilde{\psi}^k \hat{\mathbf{j}}^q(x, y, \tau)\right] d\tau. \tag{14}
$$

Hereafter we ignore the $\hat{\mathbf{v}}$ equation.

It is clear from (12) that the only surviving terms when linearizing around a *uniform* steady state correspond to the frictional interactions $(-\tilde{\phi}^i_k)$, the momentum supply rate due to reaction $(-\tilde{\psi}^i_k)$, and the acoustic term

$$
\sum_q \left(\delta_{iq} - \frac{\tilde{\rho}_i}{\tilde{\rho}}\right) \frac{\partial p^q}{\partial \rho_k}.
$$

All other terms arise only when there is a nonzero mass flux in the steady state. If one now neglects the $(\partial \mathbf{j}/\partial t)$ term in the flux relation the result is almost the simplest version of Fick's law. However, Φ is singular because $\sum_i \phi^i_k = 0$, and $\sum_i \psi^i_k = 0$, but since $\sum_{k=1}^{n+1} \hat{\mathbf{j}}^k = \mathbf{0}$ the linear dependence in the flux relations can be removed. Define

$$
\Phi'_{ik} = \Phi_{ik} - \Phi_{i,n+1} \qquad i, = 1, \ldots, n \tag{15}
$$

and hereafter drop $\hat{\mathbf{j}}^{n+1}$. Similarly, define new matrices K' and C' by dropping the $(n+1)$st row and column in each case and retaining only the $n \times n$ matrix in the upper left hand corner. This implies no loss of generality because the only nonzero terms in the last row and column of K and C are $K_{n+1,n+1}$ and $C_{n+1,n+1}$ and the equation for ρ_{n+1} is uncoupled. If we denote the truncated vectors and matrices with the same symbols, the equations at (12) read

$$
\begin{aligned}
&\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} - K\rho = 0, \\
&\frac{\partial j}{\partial t} + \Phi \mathbf{j} + C \nabla \rho = 0,
\end{aligned}
\tag{16}
$$

where ρ and $\mathbf{j}$ are now n-component vectors. Hereafter we shall assume that the $n \times n$ matrix Φ has real, distinct positive eigenvalues and that the $n \times n$ matrix C is positive definite.[14] If the term $(\partial \mathbf{j}/\partial t)$ is now dropped, the flux equation can be written $\mathbf{j} = -D \nabla \rho$, provided we define the "diffusion coefficients" as $D_{ik} = (\Phi^{-1} C)_{ik}$. This, of course, is the simplest statement of Fick's law in a multicomponent system.[15] Even so, the diffusivities D_{ik} are more general than usual in that they include the term for the momentum supply due to reaction.

In general, the second equation of (16) can be integrated with respect to time to give

$$
\mathbf{j}(x, y, t) = e^{-\Phi t} \mathbf{j}(x, y, 0) - \int_0^t e^{-\Phi(t-\tau)} C \nabla \rho(x, y, \tau)\, d\tau, \tag{17}
$$

and this shows that the present value of the flux depends on the history of the density gradients over the interval $(0, t)$. The eigenvalues of Φ are reciprocal relaxation times, and when these eigenvalues are large, the effect of the initial flux $\mathbf{j}(x, y, 0)$ decays rapidly. Under these circumstances, the major contribution to the integral comes from $t - \tau \sim 0$, and one expects that after elapse of a short time following imposition of a disturbance, the flux is approximately given by Fick's law. The conditions under which this is true are investigated in the following sections.

III. SOLUTION OF THE INITIAL BOUNDARY VALUE PROBLEM

It is convenient to reduce (16) to a second-order equation in ρ alone by eliminating $\mathbf{j}$. The result is

$$
\begin{aligned}
&\Phi^{-1} \frac{\partial^2 \rho}{\partial t^2} + (I - \Phi^{-1} K) \frac{\partial \rho}{\partial t} = D \nabla^2 \rho + K\rho, \\
&\rho(x, y, 0) = \rho_0(x, y)\,, \\
&\frac{\partial \rho}{\partial t}(x, y, 0) = -\nabla \cdot \mathbf{j}_0(x, y) + K\rho_0(x, y)\,, \\
&\mathbf{n} \cdot \nabla \rho = 0 \text{ on the boundary,}
\end{aligned}
\tag{18}
$$

where $\mathbf{n}$ is the unit normal to the boundary and $D \equiv \Phi^{-1}C$, as previously. This second-order equation is hyperbolic and the initial boundary-value problem is well posed provided that the "acoustic" matrix C is positive definite.[16] In this case there are n acoustic speeds, all finite, two or more of which may coincide. Equation (18) is a system of coupled telegrapher's equations that differs, in the absence of reaction and exchange ($K \equiv 0$), from the corresponding parabolic system obtained using Fick's law only in the term $\Phi^{-1}\partial^2\rho/\partial t^2$. However, when $K \neq 0$, the "damping" term $\partial\rho/\partial t$ is modified by a term $-\Phi^{-1}K$, and interaction between reaction and momentum exchange is directly reflected in the partial differential equation. In the case where $\Phi^{-1}K = I$, the damping term vanishes completely and one is left with a set of coupled wave equations. However, this case seems devoid of any physical significance and its occurrence is likely to be coincidental.

A suitable nondimensionalization of (18) is obtained by defining

$$\begin{aligned}
&\delta = \max_{i,j} |D_{ij}|, \quad \kappa = \max_{i,j} |\quad|, \quad \phi^{-1} = \max_{i,j} |\Phi_{ij}^{-1}|,\\
&\epsilon = \kappa/\phi, \quad \eta = x/L, \quad \zeta = y/L, \quad \tau = \kappa t,\\
&\rho^* = \max_{i,x,y} |\rho_{0i}(x,y)|, \quad j^* = \max_{i,x,y} |j_{0ix}(x,y), j_{0iy}(x,y)|, \qquad (19)\\
&\rho_i' = \rho_i/\rho^*, \quad \mathbf{j}_i' = \mathbf{j}_i/j^*, \quad D_{ij}' = D_{ij}/\delta,\\
&K_{ij}' = K_{ij}/\kappa, \quad \Phi_{ij}'^{-1} = \phi\Phi_{ij}^{-1},
\end{aligned}$$

for then the equations read

$$\begin{aligned}
&\epsilon\Phi'^{-1}\frac{\partial^2\rho'}{\partial t^2} + (I - \epsilon\Phi'^{-1}K)\frac{\partial\rho}{\partial t} = \left(\frac{\delta}{\kappa L^2}\right) D\left(\frac{\partial^2\rho'}{\partial\eta^2} + \frac{\partial^2\rho'}{\partial\zeta^2}\right) + K'\rho',\\
&\rho'(\eta,\zeta,0) = \rho_0'(\eta,\zeta),\\
&\frac{\partial\rho}{\partial\tau}(\eta,\zeta,0) = \frac{-j^*}{\rho^*\kappa L}\nabla' j' + K\rho_0',\\
&\mathbf{n}\cdot\nabla'\rho' = 0 \text{ on the boundary.}
\end{aligned} \qquad (20)$$

(Hereafter we drop the primes on all variables.) By virtue of these normalizations, all entries of ρ, Φ^{-1}, K, and D are quantities whose order of magnitude is unity. Typical values for δ are 10^{-5}–10^{-7} cm^2/sec, and κ may range from $\sim 10^{-2}$ sec^{-1} for very slow reactions to 10^4 sec^{-1} or larger for very rapid reactions. The entries of Φ are characteristic frequencies for momentum exchange and hence are of order 10^{10}–10^{12} sec^{-1}. Therefore the characteristic relaxation time ϕ^{-1} is of order 10^{-10}–10^{-12} sec.[17]

For sufficiently smooth initial data, the solution of (20) has an eigenfunction expansion

$$\rho(\eta,\zeta,\tau) = \sum_{k,l=0} y_{kl}(\tau)U_{kl}(\eta,\zeta) \qquad (21)$$

that converges uniformly along with its first two η, ζ, and τ derivatives, on $0 \le \eta, \zeta \le 1$, $\tau \ge 0$. The eigenfunctions $\{U_{kl}\}$ are complete and orthonormal; they satisfy

$$\frac{\delta}{\kappa L^2}\left(\frac{\partial^2 U_{kl}}{\partial\eta^2} + \frac{\partial^2 U_{kl}}{\partial\zeta^2}\right) = -\mu_{kl}U_{kl} \qquad (22)$$

and have zero normal derivative on the boundary. The n-component amplitude vectors $y_{kl}(\tau)$ are solutions of

$$\begin{aligned}
&\epsilon\Phi^{-1}\frac{d^2 y_{kl}}{d\tau} + (I - \epsilon\Phi^{-1}K)\frac{dy_{kl}}{d\tau} = (K - \mu_{kl}D)y_{kl},\\
&y_{kl}(0) = \alpha_{kl}, \quad \frac{dy_{kl}}{d\tau}(0) = \beta_k + K\alpha_k,
\end{aligned} \qquad (23)$$

where α_k and β_k are vectors of Fourier coefficients of the initial density and flux disturbances, respectively. To simplify notation, we hereafter drop all subscripts k and l and define $Y(\tau) = [y(\tau),\ dy(\tau)/d\tau]^T$ and

$$A = \left[\begin{array}{c|c} 0 & I \\ \hline \frac{\Phi}{\epsilon}(K - \mu D) & K - \frac{\Phi}{\epsilon} \end{array}\right],$$

and then (23) becomes

$$\begin{aligned}
&dY/d\tau = AY,\\
&Y(0) = Y_0 \equiv \begin{pmatrix} \alpha \\ \beta + K\alpha \end{pmatrix}.
\end{aligned} \qquad (24)$$

The solution of this is $Y(\tau) = e^{A\tau}Y(0)$, which in expanded form reads

$$Y(\tau) = \sum_{j=1}^{s} e^{\lambda_j\tau}\left[P_j + \lambda_j\tau N_j + \cdots \frac{(\lambda_j\tau N_j)^{M_j-1}}{(M_j-1)!}\right] Y(0). \qquad (25)$$

Here P_j is the $2n \times 2n$ projection associated with λ_j, N_j the corresponding nilpotent, s the number of distinct eigenvalues, and M_j the multiplicity of the jth eigenvalue.[18]

The eigenvalues satisfy

$$|A - \lambda I| = 0, \qquad (26)$$

or equivalently

$$|\epsilon\Phi^{-1}\lambda^2 + (I - \epsilon\Phi^{-1}K)\lambda - (K - \mu D)| = 0.$$

This determinantal equation, when expanded, yields a polynomial in λ of degree $2n$, the coefficients of which are polynomials in ϵ and μ. If (26) is irreducible, the $2n$ λ's are branches of a single algebraic function.[19] For simplicity we shall assume that these $2n$ branches are distinct for ϵ sufficiently small and every μ that is an eigenvalue of the Laplacian. At $\epsilon = 0$, (26) reduces to $|\lambda I - (K - \mu D)| = 0$, which is the characteristic equation obtained by using Fick's law as the constitutive equation for the diffusion flux.[20] By assumption, the eigenvalues of this equation, call them ω_j, are distinct. Consequently, n of the roots of (26) have the form

$$\lambda_j = \omega_j + \lambda_{j1}\epsilon + \mathcal{O}(\epsilon) \quad j = 1, \ldots, n, \qquad (27)$$

where $f(\epsilon) \sim \mathcal{O}(\epsilon)$ means

$$\lim_{\epsilon\to 0} f\frac{(\epsilon)}{\epsilon} = 0.$$

The remaining n λ's are obtained by setting $\tilde{\lambda} = \epsilon\lambda$ in (26) to get

$$|\tilde{\lambda}^2 I + \tilde{\lambda}\Phi - \epsilon\Phi(\Phi^{-1}K + K - \mu D)| = 0. \qquad (28)$$

The n $\tilde{\lambda}$'s of interest are

$$\tilde{\lambda}_j = -\Pi_j + \tilde{\lambda}_{j1}\epsilon + \mathcal{O}(\epsilon) \quad j = n+1, \ldots, 2n,$$

where the Π_j are the eigenvalues of Φ. Consequently, the $2n$ roots of (26) have the form

$$\lambda_j = \omega_j + \lambda_{j1}\epsilon + \mathcal{O}(\epsilon) \qquad j = 1, \ldots, n ,$$
$$\lambda_j = \frac{-\Pi_j}{\epsilon} + \tilde{\lambda}_{j1} + \mathcal{O}(1) \qquad j = n+1, \ldots, 2n . \tag{29}$$

Clearly n of these have a pole at $\epsilon = 0$, while the remaining n are analytic there.

Because the eigenvalues are assumed to be distinct, both A and its adjoint A^T, have a complete set of eigenvectors, the nilpotents N_j are zero, [21] and (25) reduces to

$$Y(\tau) = \sum_j e^{\lambda_j \tau} P_j Y_0 . \tag{30}$$

Let X be a $2n$-dimensional unitary space with inner product $\langle x, y\rangle_2 \equiv \sum_{i=1}^{2n} x_i y_i$, let $\{u_1, \ldots, u_n\}$ be the eigenvectors of A, and $\{v_1, \ldots, v_n\}$ the eigenvectors of its adjoint. We choose the u's and v's so that they are biorthogonal; $\langle v_j, u_k\rangle_2 = \delta_{jk}$. The P_j's are of rank one, and consequently each may be written $P_j = u_j * v_j$ where $*$ is a dyad product. This product is defined operationally by $P_j u = \langle v_j, u\rangle u_j$ for any $u \in X$.

The eigenvectors u_j are solutions of $(A - \lambda_j I)u_j = 0$, and the v_j are solutions of $(A^T - \bar{\lambda}_j I)v_j = 0$. In expanded form

$$\left[\begin{array}{c|c} -\lambda_j I & I \\ \hline \frac{\Phi}{\epsilon}(K - \mu D) & K - \frac{\Phi}{\epsilon} - \lambda_j I \end{array}\right] \cdot \left[\begin{array}{c} u_j^{\mathrm{I}} \\ \hline u_j^{\mathrm{II}} \end{array}\right] = 0 \tag{31}$$

and

$$\left[\begin{array}{c|c} -\bar{\lambda}_j I & (K - \mu D)^T \frac{\Phi^T}{\epsilon} \\ \hline I & K^T - \frac{\Phi^T}{\epsilon} - \bar{\lambda}_j I \end{array}\right] \cdot \left[\begin{array}{c} v_j^{\mathrm{I}} \\ \hline v_j^{\mathrm{II}} \end{array}\right] = 0$$

when u_j and v_j are partitioned in conformance with A. From these equations one finds that the eigenvectors can be written in terms of the n-component eigenvectors $u^{K-\mu D}$, $v^{K-\mu D}$ and u^{Φ}, v^{Φ} of $K - \mu D$ and Φ, respectively, as follows:

$$u_j = \begin{pmatrix} u_j^{K-\mu D} + \mathcal{O}(\epsilon) \\ \omega_j u_j^{K-\mu D} + \mathcal{O}(\epsilon) \end{pmatrix} \qquad j = 1, \ldots, n$$
$$u_j = \begin{pmatrix} u_j^{\Phi} + \mathcal{O}(\epsilon) \\ \frac{-\Pi_j}{\epsilon} u_j^{\Phi} + \mathcal{O}(1) \end{pmatrix} \qquad j = n+1, \ldots, 2n , \tag{32}$$

$$v_j = \begin{pmatrix} v_j^{K-\mu D} + \mathcal{O}(\epsilon) \\ \epsilon(\Phi^{-1})^T v_j^{K-\mu D} + \mathcal{O}(\epsilon^2) \end{pmatrix} \qquad j = 1, \ldots, n ,$$
$$v_j = \frac{1}{\mathfrak{N}_j} \begin{pmatrix} -(K - \mu D)^T v_j^{\Phi} + \mathcal{O}(\epsilon) \\ v_j^{\Phi} + \mathcal{O}(\epsilon) \end{pmatrix} \qquad j = n+1, \ldots, 2n . \tag{33}$$

Here $\mathcal{O}(\epsilon^n)$ represents quantities $f(\epsilon)$ for which

$$\lim_{\epsilon \to 0} \frac{f(\epsilon)}{\epsilon^n}$$

is bounded and the $\mathfrak{N}_j$ are normalization factors that ensure that

$$\langle v_j, u_k\rangle_2 = \delta_{jk} \qquad j, k = 1, \ldots, 2n$$

for all $\epsilon \neq 0$. It is consistent with this normalization to biorthogonalize the sets $\{u_j^{\Phi}, v_j^{\Phi}\}$ and $\{u_j^{K-\mu D}, v_j^{K-\mu D}\}$ as n-component vectors and this is done hereafter.

It follows from the definition of the projections as dyad products, that $u * R^T v = (u * v)R$ for any $n \times n$ matrix R. Using this fact, P_j can be written

$$P_j = \left[\begin{array}{c|c} P_j^{K-\mu D} + \epsilon P_{j1}(\epsilon) & \epsilon\{P_j^{K-\mu D}\Phi^{-1} + \epsilon P_{2j}(\epsilon)\} \\ \hline \omega_j(P_j^{K-\mu D} + \epsilon P_{j1}(\epsilon)) & \epsilon\omega_j\{P_j^{K-\mu D}\Phi^{-1} + \epsilon P_{2j}(\epsilon)\} \end{array}\right] \qquad j = 1, \ldots, n$$
$$P_j = \frac{1}{\mathfrak{N}_j}\left[\begin{array}{c|c} -P_j^{\Phi}(K - \mu D) + \epsilon P_{j3}(\epsilon) & P_j^{\Phi} + \epsilon P_{j4}(\epsilon) \\ \hline \frac{\Pi_j}{\epsilon}\{P_j^{\Phi}(K - \mu D) + \epsilon P_{j3}(\epsilon)\} & -\frac{\Pi_j}{\epsilon}\{P_j^{\Phi} + \epsilon P_j^{\Phi} + \epsilon P_{j4}(\epsilon)\} \end{array}\right] \qquad j = n+1, \ldots, 2n, \tag{34}$$

where the matrices $P_j^{K-\mu D}$ and P_j^{Φ} are the $n \times n$ projections corresponding to the eigenvalues ω_j and Π_j of $K - \mu D$ and Φ, respectively. All entries of the matrices $P_{jk}(\epsilon)$, $k = 1, \ldots, 4$ are $\mathcal{O}(1)$ quantities. Since $\{u, v_j\}$ is biorthogonal, the P_j satisfy $P_j P_k = \delta_{jk} P_k$.

If we formally set $\epsilon = 0$ in the first n projections, we get

$$P_j^0 = \left[\begin{array}{c|c} P_j^{K-\mu D} & 0 \\ \hline \omega_j P_j^{K-\mu D} & 0 \end{array}\right] \qquad j = 1, \ldots n . \tag{35}$$

For any vector

$$\begin{pmatrix} u \\ v \end{pmatrix} \in X ,$$

u, v n-dimensional,

$$P_j^0 \begin{pmatrix} u \\ v \end{pmatrix} \propto \begin{pmatrix} u_j \\ \omega_j u_j \end{pmatrix} ,$$

which of course is proportional to the eigenvector in (32). The union of the n one-dimensional manifolds spanned by vectors of the form

$$\begin{pmatrix} u_j \\ \omega_j u_j \end{pmatrix}$$

is an n-dimensional subspace U^0 of X, and when $\epsilon = 0$, the vector

$$\begin{pmatrix} y \\ \dot{y} \end{pmatrix}$$

is confined to U^0. From (34) one can see that when $\epsilon \neq 0$

$$\begin{pmatrix} y \\ \dot{y} \end{pmatrix}$$

is no longer confined to U^0 because the projections P_j $j=1, \ldots, n$ are no longer projections onto U^0. In fact, the first-order effect of the perturbation is twofold. The eigenvectors u_j, $j=1, \ldots, n$ are different by an $\mathcal{O}(\epsilon)$ quantity and hence the corresponding projections P_j are projections onto a subspace U^1 that is different from U^0. Secondly, the solution now also has a component in an n-dimensional subpace U^2 that is complementary to U^1. U^2 is spanned by the eigenvectors u_j, $j=n+1, \ldots, 2n$ and the projections P_j $j=n+1, \ldots, 2n$ are projections onto U^2.

The first-order effect on the amplitudes $y(\tau)$ can be found by using the projections at (34) in (30); the result is

$$y(\tau) = \sum_{j=1}^{n} \exp\{[\omega_j + \mathcal{O}(\epsilon)]\tau\}\,[P_j^{K-\mu D} + \epsilon(P_{j1} + P_j^{K-\mu D}\Phi^{-1}K)]\alpha + \sum_{j=n+1}^{2n} \exp\left(\left[-\frac{\pi_j}{\epsilon} + \mathcal{O}(1)\right]\tau\right)[-P_j^{\Phi}(K-\mu D) + \epsilon(P_{j3} + P_j^{\Phi}K)]\,\alpha$$
$$+ \epsilon \sum_{j=1}^{n} \exp\{[\omega_j + \mathcal{O}(\epsilon)]\tau\} P_j^{K-\mu D}\Phi^{-1}\beta + \epsilon \sum_{j=n+1}^{2n} \exp\left(\left[-\frac{\pi_j}{\epsilon} + \mathcal{O}(1)\right]\tau\right) P_j^{\Phi}\beta\,. \tag{36}$$

By comparison, if ϵ is taken to be identically zero at the outset, the result is

$$y(\tau) = \sum_{j=1}^{n} e^{\omega_j \tau} P_j^{K-\mu D}\alpha, \tag{37}$$

which coincides with the first term in the first summation of (36), but for the $\mathcal{O}(\epsilon)$ difference in the eigenvalues.

The solutions (36) and (37) differ qualitatively in several ways. First, the density disturbance is coupled to the initial flux disturbance via the third and fourth terms of (36). In the extreme case of $\alpha = 0$, $\beta \neq 0$, (37) predicts that there is no disturbance whatsoever, while (36) predicts that $y(\tau) \sim \mathcal{O}(\epsilon)$ for $\tau > 0$ if all $\omega_j + \mathcal{O}(\epsilon)$ have negative real parts. Secondly, (36) contains components in U^2, given by the second and fourth terms. If all $\pi_j \gg \epsilon$, these components decay rapidly and are significant only for $t < \epsilon/\min_j\{\pi_j\}$. Both U^1 and U^2 are invariant subspaces for (24), but given an initial point in neither U^1 nor U^2, the solution rapidly approaches U^1 and then evolves along a trajectory close to U^1 on a much longer time scale. This is a standard phenomenon in a singularly-perturbed problem. However, it should be emphasized that U^1 is not U^0, and the time evolution of a point

$$\begin{pmatrix} y(\tau) \\ \dot{y}(\tau) \end{pmatrix}$$

on or near U^1 may be significantly different from that on U^0. Some examples in the following section illustrate this.

An analogous comparison can be made for the fluxes. The dimensionless form of (17) is

$$\mathbf{j}(\eta, \zeta, \tau) = e^{-(\Phi/\epsilon)\tau}\mathbf{j}_0(\eta, \zeta) - \chi \int_0^{\tau} e^{-(\Phi/\epsilon)(\tau-\tau')} \frac{\Phi}{\epsilon} \nabla\rho\, d\tau', \tag{38}$$

where $\chi \equiv \delta\rho^*/(j^* L)$. After integration by parts and rearrangement this yields

$$\mathbf{j}(\zeta, \eta, \tau) = -\chi D\nabla\rho + e^{-(\Phi/\epsilon)\tau}[\mathbf{j}_0(\zeta, \eta) - (-\chi D\nabla\rho_0)]$$
$$+ \chi\nabla\left[\int_0^{\tau} e^{-(\Phi/\epsilon)(\tau-\tau')} D\frac{\partial\rho}{\partial\tau'} d\tau'\right]. \tag{39}$$

The first term is the Fick's law flux at time τ and the second the initial ($\tau = 0$) discrepancy between the specified flux and that calculated by Fick's law. The third term represents the effect of including the finite relaxation time, for $\tau > 0$. As before, the second term decays rapidly, leaving the Fick's law component and the integral term. One can readily show, using the series expansion for ρ in (39), that if all the perturbed eigenvalues are negative or have a negative real part, the integral term is $\mathcal{O}(\epsilon)$ for $\tau > 0$ and the flux is closely approximated by Fick's law.

If it were physically meaningful to let $\epsilon \to 0$, we would conclude from (36) and (40) that the amplitudes $y(\tau)$ and fluxes $\mathbf{j}(\zeta, \eta, \tau)$ of the nondegenerate ($\epsilon \neq 0$) system approach those of the degenerate ($\epsilon = 0$) system uniformly in τ as $\epsilon \to 0$, provided τ is bounded away from zero. But physical considerations dictate that ϵ, though small, is strictly positive and hence we must determine how much the eigenvalues of the nondegenerate system differ from those of the degenerate system. This is done in the following section by calculating the leading order terms in the functions represented by $\mathcal{O}(\epsilon)$ in (27) and (32).

IV. COMPARISON OF STABILITY FOR HYPERBOLIC AND PARABOLIC SYSTEMS

The eigenvalues of the n "fast" modes in U^2 are large and negative for small ϵ, and we shall assume that the relative first-order correction to these eigenvalues and the corresponding eigenvectors is negligible. The remaining eigenvalues and eigenvectors are analytic in ϵ for small ϵ, and the first-order corrections can be computed by a straightforward perturbation expansion. As before, $u_j = (u_j^{\mathrm{I}}, u_j^{\mathrm{II}})$ and $v_j = (v_j^{\mathrm{I}}, v_j^{\mathrm{II}})$ $j=1, \ldots, n$, and, from (31), $u_j^{\mathrm{II}} = \lambda_j u_j^{\mathrm{I}}$ and $v_j^{\mathrm{I}} = (K - \mu D)^T \Phi^T v_j^{\mathrm{II}}/\epsilon\bar{\lambda}_j$. Thus the equations for u_j^{I} and v_j^{II} can be written

$$[K - \mu D - \lambda_j I + \epsilon\lambda_j \Phi^{-1}(K - \lambda_j I)]\,u_j^{\mathrm{I}} = 0,$$

$$[(K-\mu D)^T\Phi^T+\bar{\lambda}_j(\epsilon K^T-\Phi^T)-\epsilon\bar{\lambda}_j^2]v_j^{II}=0. \tag{40}$$

Define

$$L_0(\lambda)=K-\mu D-\lambda_j I,$$
$$L_1(\lambda)=\lambda_j\Phi^{-1}(K-\lambda_j I),$$

and write

$$\lambda_j(\epsilon)=\omega_j+\epsilon\lambda_{j1}+\epsilon^2\lambda_{j2}+\cdots,$$
$$u_j^I(\epsilon)=u_{j0}+\epsilon u_{j1}+\epsilon^2 u_{j2}+\cdots, \tag{41}$$
$$v_j^{II}(\epsilon)=\epsilon v_{j1}+\epsilon^2 v_{j2}+\cdots,$$

where $u_{j0}\equiv u_j^{K-\mu D}$ and $v_{j1}\equiv(\Phi^{-1})^T v_j^{K-\mu D}$. The equation for $u_j^I(\epsilon)$ can now be written

$$[L_0(\lambda)+\epsilon L_1(\lambda)]u_j^I=0, \tag{42}$$

and after inserting the series and equating coefficients of like powers of ϵ there results the sequence of relations

$$L_0(\omega_j)u_{j0}=0,$$
$$L_0(\omega_j)u_{j1}=[\lambda_{j1}I-L_1(\omega_j)]u_{j0}, \tag{43}$$

The first of these is satisfied identically since $u_{j0}=u_j^{K-\mu D}$ is the eigenvector of $K-\mu D$ that corresponds to the eigenvalue ω_j. Because L_0 is singular, the Fredholm alternative[22] implies that the second equation has no solution unless the right-hand side is orthogonal to all solutions of the adjoint equation

$$[K^T-\mu D^T-\bar{\omega}_j I]v=0. \tag{44}$$

This has only one solution, $v_{j0}\equiv v_j^{K-\mu D}$, and consequently the orthogonality condition can be written

$$\langle v_{j0},\ (\lambda_{j1}I-L_1(\omega_j))u_{j0}\rangle_1=0. \tag{45}$$

This can be solved for λ_{j1}, the first-order correction, to give

$$\lambda_{j1}=\langle v_{j0},\ L_1(\omega_j)u_{j0}\rangle$$
$$=\omega_j\langle v_{j0},\ \Phi^{-1}(K-\omega_j I)u_{j0}\rangle$$
$$=\mu\omega_j\langle v_{j0},\ \Phi^{-1}Du_{j0}\rangle,\qquad j=1,\ \ldots,\ n. \tag{46}$$

(Here and hereafter all inner products are in n-dimensional space.) However, not all λ_{j1} are independent, because it follows from (26) that the constant term divided by the coefficient of λ^{2n} is $[\det(K-\mu D)\det\Phi]/(-\epsilon^n)$. This must equal the product of all $2n$ eigenvalues,

$$\prod_{i=1}^{2n}\lambda_i=\frac{\det(K-\mu D)\det\Phi}{(-\epsilon^n)}, \tag{47}$$

and if we let λ_{k0} stand for either ω_k or $-\Pi_k$, it can be shown that

$$\sum_{k=1}^{2n}\lambda_{k1}\left(\prod_{\substack{j=1\\ j\neq k}}^{2n}\lambda_{j0}\right)=0.$$

Therefore, if neither $K-\mu D$ or Φ has any zero eigenvalues, it is necessary that

$$\sum_{k=1}^{2n}(\lambda_{k1}/\lambda_{k0})=0. \tag{48}$$

If, for instance, all λ_{k0} are negative, then some eigenvalues must decrease and some must increase. In particular, it can never happen that there is only one eigenvalue for which λ_{k1} is very large, while all other λ_{k1} are small.

As already noted, $L_0(\omega_j)$ is singular, and therefore to find u_{j1} from (43b) requires a generalized inverse or generalized Green's function.[23] This satisfies

$$L_0G_j=I-u_{j0}*v_{j0} \tag{49}$$

and is given by

$$G_j=\sum_{\substack{i=1\\ i\neq j}}^{n}\frac{u_{i0}*v_{i0}}{\omega_i-\omega_j}=\sum_{\substack{i=1\\ i\neq j}}^{n}\frac{P_i^{K-\mu D}}{\omega_i-\omega_j},$$

where subscript j indicates that this is the Green's function for a perturbation of the jth eigenvalue. The solution of (43b) is only determined to within an arbitrary additive vector parallel to u_{j0}. It can be written

$$u_{j1}=\sum_{\substack{i=1\\ i\neq j}}^{n}\left(\frac{P_i^{K-\mu D}}{\omega_i-\omega_j}\right)\{\lambda_{j1}I-L_1(\omega_j)\}u_{j0}+cu_{j0}, \tag{50}$$

where c is an arbitrary constant. If we require that $\langle v_{j0},\ u_{j1}\rangle=0$, then $c\equiv 0$ and u_{j1} is uniquely determined. After simplification of (50), one gets

$$u_{j1}=\omega_j\mu\sum_{\substack{i=1\\ i\neq j}}^{n}\frac{\langle v_{i0},\ \Phi^{-1}Du_{j0}\rangle u_{i0}}{\omega_i-\omega_j}. \tag{51}$$

The first-order correction for the adjoint eigenvector is constructed in an analogous manner. Higher-order terms in the series are calculated by repeating the foregoing procedure. For example, the second-order term for an eigenvalue is

$$\lambda_{j2}=\mu\omega_j^2\sum_{\substack{i=1\\ i\neq j}}^{n}\langle v_{i0},\Phi^{-1}Du_{j0}\rangle\left\{\langle v_{j0},\Phi^{-1}u_{i0}\rangle+\frac{\mu}{\omega_i-\omega_j}\langle v_{j0},\ \Phi^{-1}Du_{j0}\rangle\right\}-\mu\omega_j^2\langle v_{j0},\ \Phi^{-1}u_{j0}\rangle\langle v_{j0},\ \Phi^{-1}Du_{j0}\rangle+\mu^2\omega_j\langle v_{j0},\ \Phi^{-1}Du_{j0}\rangle^2. \tag{52}$$

Both the eigenvalue and eigenvector corrections are proportional to the dimensionless wavenumber μ, raised to some power, and hence both vanish at zero wavenumber (infinite wavelength) and are most important at large wavenumbers (short wavelengths). To determine the magnitude of the relative correction, $\epsilon\lambda_{j1}/\omega_j$, define vector and matrix norms

$$\|x\|\equiv(\langle x,x\rangle)^{1/2},$$
$$\|A\|=\sup_{\|x\|=1}\|Ax\| \tag{53}$$

for n-component vectors and $n\times n$ matrices, respectively. It can be shown that $\|A\|$ equals the largest eigenvalue of AA^* and that if $|A_{ij}|\leq 1$, then $\|A\|\leq n$.[24]

It then follows from (46), by use of Schwarz' inequality, that

$$\left|\frac{\lambda_{j1}}{\omega_j}\right| = \mu\left|\langle v_{j0},\ \Phi^{-1}Du_{j0}\rangle\right|$$
$$\leq \mu\|\Phi^{-1}\|\cdot\|D\|\cdot\|v_{j0}\|\cdot\|u_{j0}\|$$
$$\leq \mu n^2\|v_{j0}\|\cdot\|u_{j0}\|\,. \tag{54}$$

This upper bound is the best possible for arbitrary Φ and D within the class considered here, because equality can hold for special choices of Φ and D.

When $K-\mu D$ is self-adjoint (symmetric), the adjoint eigenvectors v_{j0} coincide with the u_{j0}, and the latter can be chosen so that $\|u_{j0}\|=1$. The above inequality then reduces to $|\lambda_{j1}/\omega_j|\leq\mu n^2$, and therefore the relative magnitude of the first-order term $\epsilon\lambda_{j1}$ is bounded above by $\epsilon\mu n^2$. A continuum model of diffusion would surely break down if the disturbance wavelength is less than 10 Å, and when this is used as a lower bound, one finds the following necessary condition from (22):

$$\frac{\kappa\mu}{\delta} < \frac{4\Pi^2}{100}\,. \tag{55}$$

Using previous estimates of κ and δ, the largest possible μ is for $\delta\sim10^{-5}$ and $\kappa\sim10^{-2}$ and then $\mu<\sim10^{12}$. For this value of κ, $\epsilon\sim10^{-12}$–10^{-14} and therefore $(\epsilon\mu)_{\max}\sim0.01$–$1.0$. Consequently, even if n is only 2 or 3, the relative correction is significant at very short wavelengths. Since particular choices of Φ may lead to values of ϕ^{-1} much larger than those used here [cf. (17)], the first-order terms can sometimes be significant even at wavelengths of ~ 100 Å. However, the corrections will be negligible, almost without exception, whenever the wavelength exceeds 1000 Å.

When $K-\mu D$ is not symmetric, the adjoint eigenvectors v_{j0} are distinct from the eigenvectors u_{j0}, and since we have chosen $\langle v_{j0},\ u_{k0}\rangle=\delta_{jk}$, the norms of v_{j0} and u_{j0} cannot be set equal to 1. They are bounded *below* by 1,[25] but cannot be bounded above *a priori*; they simply have to be calculated. In fact, it is easy to see that the norms can be made as large as desired, simply by demanding that $K-\mu D$ have two eigenvectors that are nearly parallel. By prior assumption, the eigenvalues of $K-\mu D$ are distinct and therefore two eigenvectors are never precisely parallel, but the angle between them can be made as small as desired. The consequence is that when $K-\mu D$ is not symmetric, the correction terms can be significant for all wavelengths and the eigenvalues of (26) may differ substantially from those of $K-\mu D$. In such cases, the series would converge very slowly and would be of little value for calculating the λ's.

Estimates of the magnitude of the correction to the eigenvectors u_j are gotten by analogous methods. One can readily show that when $K-\mu D$ is symmetric, the angle Θ_j between the eigenvectors u_{j0} and $u_{j0}+\epsilon u_{j1}$ satisfies

$$\cos\Theta_j = \frac{1}{1+\epsilon^2\|u_{j1}\|^2} \tag{56}$$

and is small except when $\|u_{j1}\|^2$ is large. Except at very short wavelengths, each eigenvector is only rotated slightly and therefore U^1 essentially coincides with U^0. However, at long wavelengths they may differ significantly.

The foregoing expansions show when the eigenvalues of the n "slow" modes of the hyperbolic system can differ significantly from the corresponding eigenvalues of $K-\mu D$. However, it is generally impractical to determine from these expansions whether the eigenvalues (when they are real) or their real part (when they are complex) increase or decrease as ϵ increases from zero. Consequently, it cannot be decided *a priori* whether inclusion of the relaxation time qualitatively changes the stability predicted for uniform solutions. Conceivably, the effect of relaxation could be to make a negative eigenvalue positive (or *vice-versa*), or to change the real part of a complex eigenvalue from negative to positive (or *vice-versa*). Next we show that the latter is possible while the former is impossible.

In expanded form, the characteristic equation (26) reads

$$P_{2n}\lambda^{2n}+P_{2n-1}\lambda^{2n-1}\cdots+P_1\lambda+P_0=0\,, \tag{57}$$

where all P_k are real and $P_{2n}>0$. All eigenvalues λ have negative real parts if the Hurwitz determinants

$$H_1=P_{2n-1}\,,$$
$$H_2=\begin{vmatrix}P_{2n-1} & P_{2n-3}\\ P_{2n} & P_{2n-2}\end{vmatrix}\,,$$
$$\vdots$$
$$H_n=\begin{vmatrix}P_{2n-1} & P_{2n-3} & P_{2n-5} & \cdots & 0\\ P_{2n} & & & & \vdots\\ 0 & & & & \\ \vdots & & & & 0\\ 0 & \cdots & \cdots & 0 & P_0\end{vmatrix} \tag{58}$$

are all positive.[26] When the largest real eigenvalue or the real part of any complex eigenvalue is zero, $H_1>0$, $H_2>0,\ldots,H_{2n-2}>0$, and $H_{2n}=0$.[27] Since $H_{2n}=P_0\times H_{2n-1}$, either or both of P_0 and H_{2n-1} vanish when H_{2n} vanishes. The vanishing of P_0 implies that there is a zero real eigenvalue; this case will be analyzed first.

By assumption, Φ is nonsingular and it follows from (47) that $\lambda=0$ is a solution of (57) if and only if $K-\mu D$ is singular. Therefore, the locus of marginal *stationary* stability ($\lambda=0$) in parameter space is unchanged by the inclusion of a finite, nonzero relaxation time. Throughout we have assumed that all eigenvalues of both $K-\mu D$ and A are distinct, i.e., there are no branch points of any λ in $[0,\epsilon]$. Consequently, an eigenvalue that is real at $\epsilon=0$ can never cross the locus $\lambda=0$ because $\partial\lambda/\partial\epsilon|_{\lambda=0}=0$. Thus, *whenever $K-\mu D$ has only real eigenvalues, inclusion of relaxation can neither stabilize an unstable system nor destabilize a stable system.* In particular, this pertains when $K-\mu D$ is symmetric.

When $K-\mu D$ has complex eigenvalues, it must be determined whether any eigenvalues cross the locus $H_{2n-1}=0$ as ϵ increases from zero. The following ex-

ample of a two-component system shows that this can occur. The coefficients $P_4, P_3, \ldots$ are[28]

$$
\begin{aligned}
P_4 &= \epsilon^2 t^{\Phi^{-1}}, \\
P_3 &= \epsilon T^{\Phi^{-1}} - \epsilon^2 T^K t^{\Phi^{-1}}, \\
P_2 &= \epsilon^2 t^{\Phi^{-1}} t^K - \epsilon T^K T^{\Phi^{-1}} + \epsilon\mu(T^D T^{\Phi^{-1}} - T^{D\Phi^{-1}}) + 1, \\
P_1 &= \epsilon t^K T^{\Phi^{-1}} + \epsilon\mu(T^{D\Phi^{-1}K} - T^D T^{\Phi^{-1}K}) - T^K + \mu T^D, \\
P_0 &= t^{K-\mu D},
\end{aligned}
\tag{59}
$$

where $T^C \equiv \mathrm{Tr}\, C = \sum C_{ii}$ and $t^C \equiv \det C$ denote the similarity invariants of the 2×2 matrix C. At $\epsilon = 0$, the coefficients reduce to $P_k(0) = P_k^0$, where $P_4^0 = P_3^0 = 0$, $P_2^0 = 1$, $P_1^0 = \mu T^D - T^K$, and $P_0^0 = t^{K-\mu D}$. These are the coefficients of the characteristic equation $\det(K - \mu D - \lambda I) = 0$, and this equation has roots with negative real parts for all $\mu > 0$ provided $t^{K-\mu D} > 0$ and $\mu T_1^D - T^K > 0$. We want to show that H_3 can be made negative while $P_4 > 0$, $H_1 > 0$, $H_2 > 0$, $t^{K-\mu D} > 0$ and $\mu T_1^D - T_1^K > 0$.

Since Φ (and therefore Φ^{-1}) is assumed to have only real positive eigenvalues, the invariants of Φ^{-1} must satisfy $t^{\Phi^{-1}} > 0$ and $T^{\Phi^{-1}} > 2(t^{\Phi^{-1}})^{1/2} > 0$. In order that $t^{K-\mu D}$ and $\mu T_1^D - T_1^K$ be positive, it is necessary and sufficient that[29] $T^K < 0$, $t^K > 0$, $T^D > 0$, $t^D > 0$, and $T^{KD} - T^K T^D > -2(t^K t^D)^{1/2}$. From (58) it follows that

$$
\begin{aligned}
H_1 &= P_3, \\
H_2 &= P_2 P_3 - P_1 P_4, \\
H_3 &= P_1(P_2 P_3 - P_1 P_4) - P_0 P_3^2,
\end{aligned}
\tag{60}
$$

and by virtue of the foregoing conditions on the invariants, H_1 is always positive. Since $P_1 P_4 \sim \mathcal{O}(\epsilon^2)$ and $P_2 P_3 \sim \mathcal{O}(1)$, it is clear that $H_2 > 0$ for small ϵ. For the same reason, $P_1 P_4$ can be neglected relative to $P_2 P_3$ in H_3, and to make $H_3 < 0$ we need

$$
P_3(P_1 P_2 - P_0 P_3) < 0. \tag{61}
$$

To first order in ϵ, this requires that

$$
T^{\Phi^{-1}} - \epsilon\mu t^{\Phi^{-1}} T^D < 0. \tag{62}
$$

Since the invariants of Φ^{-1} and D are all of order 1, by virtue of the chosen normalizations, it is clear that when $\epsilon\mu \sim \mathcal{O}(1)$, Eq. (62) will be satisfied. The previous estimates of parameters show that $\epsilon\mu \sim \mathcal{O}(1)$ is within the realm of physically meaningful values. Consequently, the fourth-order equation obtained by including relaxation can have a pair of roots with positive real parts, even if the roots of the second-order equation have negative real parts.

The foregoing predicts that stability is different only at very short wavelengths, but a more careful analysis of the order of magnitude of the quantities involved shows that H_3 can be made negative under less severe conditions on μ. Furthermore, when three or more chemical species are present, it can be shown that the $2n$-1st Hurwitz determinant of the $2n$-dimensional system involves additional invariants that are independent of those that appear in the n-1st determinant for the n-dimensional system. These new invariants, which arise from products of Φ^{-1}, D, and K, provide additional degrees of freedom that can be used to make H_{2n-1} negative.

In summary, the perturbation analysis shows that when $K - \mu D$ is symmetric, the eigenvalues are insensitive to inclusion of diffusion relaxation except at very short wavelengths. If in addition to $K - \mu D$ being symmetric, no eigenvalues have branch points in $[0, \epsilon]$, analysis of the characteristic equation shows that stability is qualitatively unchanged at all wavelengths by inclusion of relaxation. On the other hand, when $K - \mu D$ is not symmetric, the perturbation analysis shows that the eigenvalues can vary rapidly with ϵ at all wavelengths whenever $K - \mu D$ has a pair of eigenvectors that are "almost" parallel. In such cases, it follows from Eq. (46) that there can be large differences, at any wavelength, between the frequency of oscillation and the decay or growth rate calculated for the "perturbed" system ($\epsilon \neq 0$) and those calculated for the unperturbed ($\epsilon = 0$) system. Moreover, analysis of the characteristic equation shows that stability in the two systems can be qualitatively different as well, at least to the extent that a system predicted to be stable for $\epsilon = 0$ can be unstable for $\epsilon \neq 0$. Whether a system unstable for $\epsilon = 0$ can be stable for $\epsilon \neq 0$ has not been investigated.

V. CONCLUSION

The foregoing results bring out a fundamental difference between monotonic and oscillatory growth or decay of disturbances in multicomponent systems. To zero order in the disturbance amplitude, (i.e., in the linear analysis), the inertia effects that give rise to higher-order time derivatives have little effect on growth or decay rates and can never qualitatively change stability when growth or decay is monotonic. However, the same inertia terms can significantly change both growth or decay rate and frequency for oscillatory modes. Evidently this difference arises only in multicomponent systems, since at least two species are required to produce a pair of complex conjugate roots to the characteristic equation. Consequently, use of Fick's law in a multicomponent system will not lead to accurate predictions of stability behavior in all cases. When numerical data on Φ, D, and K are available, the characteristic equation with $\epsilon \neq 0$ should be solved, at least whenever $K - \mu D$ has complex conjugate eigenvalues.

Further analysis of the constitutive equations is required to determine what, if any, restrictions on the structure of the equations are implied by the requirement of a nonnegative entropy production rate.[30] This has not been pursued here because we have treated only linearized versions of the constitutive equations. An analysis of such conditions for a limited class of nonreacting systems is given by Müller.[31]

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