SIAM J. APPL. MATH.
Vol. 28, No. 2, March 1975

OSCILLATORY PROCESSES IN THE THEORY OF PARTICULATE FORMATION IN SUPERSATURATED CHEMICAL SOLUTIONS*

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Abstract. We study a nonlinear problem which occurs in the theory of particulate formation in supersaturated chemical solutions. Mathematically, the problem involves the bifurcation of time-periodic solutions in an initial-boundary value problem involving a nonlinear integro-differential equation. The mechanism controlling the oscillatory states is revealed by combining the theory of characteristics for first order partial differential equations with the multi-time scale perturbation analysis of a certain third order system of nonlinear ordinary differential equations.

1. Introduction. This paper was stimulated by a nonlinear problem which has recently arisen in the theory of particulate formation in supersaturated chemical solutions. We shall treat it and some mathematical generalizations of it here.

The specific problem which motivated our study is that of finding time-periodic solutions of the nonlinear integro-differential equation

$$\frac{\partial y}{\partial t} + \frac{2}{\int_0^\infty x^2 y(x,t)\,dt}\frac{\partial y}{\partial x} + y = 0, \qquad x > 0, \quad t > 0, \tag{1.1}$$

$$y(0,t) = \frac{1}{[\frac{1}{2}\int_0^\infty x^2 y(x,t)\,dx]^p}, \qquad t > 0, \tag{1.2}$$

$$y(x,0) = f(x), \qquad x \geqq 0. \tag{1.3}$$

In § 2 we shall derive this problem from the governing fundamental chemical principles.

The key step in the analysis of this problem will be to obtain and analyze a certain system of nonlinear ordinary differential equations (the moment equations) for the moment functions $m_k(t)$, $k = 1, 2, 3$, defined by

$$m_k(t) = \frac{1}{k!}\int_0^\infty x^k y(x,t)\,dx. \tag{1.4}$$

The system of moment equations is obtained in § 3 where its importance and use will also be explained. The study of the moment equations led us to investigate the following general system of nonlinear ordinary differential equations:

$$\frac{dX}{dt} = PX + \varepsilon^2 AX + g(X). \tag{1.5}$$

Here X is a three-component vector, P and A are constant matrices, $g(X)$ is a smooth nonlinear function containing no linear terms, and $0 < \varepsilon \ll 1$. In § 4 we analyze (1.5) specifically for oscillatory solutions. This is accomplished formally by a multi-time scale perturbation method. Not only does this method produce

* Received by the editors November 23, 1973.

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the periodic solutions but the stability of the solutions is also immediately resolved without recourse to further techniques.

Finally, in § 5 we investigate our main problem (1.1)–(1.3). By coupling our theory of §§ 3 and 4 with the theory of characteristics for first order partial differential equations we are able to demonstrate the existence of periodic solutions of (1.1)–(1.3) when p is increased slightly beyond its critical (or bifurcation) value $p^* = 20$. Furthermore, our multi-time scale perturbation analysis yields the entire time history of the solution $y(x, t)$ of (1.1)–(1.3) and its manner of approach to the periodic state.

2. Equations of state. We shall consider the process of particulate formation in a large vat of thoroughly mixed supersaturated solution. Let R be a characteristic size (e.g., the radius) of a given particle, and let $n(R, \tau)$ be the number of particles of size R per unit volume of solution at time τ. (The assumption of a thoroughly mixed solution implies that all quantities will have no spatial dependence. We shall point out further implications of this and other assumptions later.)

Using an Eulerian coordinate description, we have

$$\frac{d}{d\tau}\iiint_V n(R, \tau)\, dR = \iiint_V [B(R, \tau) - D(R, \tau)]\, dR - \iint_S [n(R, \tau)G]_N\, dS, \tag{2.1}$$

where $B(R, \tau)$ and $D(R, \tau)$ represent the birth and death rates per unit volume, respectively, of particles of size R at time τ, V is some arbitrary region of R-space with surface S, and the subscript N denotes the normal component of flux across the boundary. Using the divergence theorem, we conclude in the usual manner that (2.1) implies

$$\frac{\partial n}{\partial \tau} + \nabla \cdot (Gn) - B + D = 0. \tag{2.2}$$

The term $G(R, n)$ represents the rate of growth of a particle of size R. An empirical observation known as McCabe's law states that the growth rate G is independent of size, so that $\partial G/\partial R = 0$. Thus, (2.2) becomes

$$\frac{\partial n}{\partial \tau} + G\frac{\partial n}{\partial R} - B + D = 0. \tag{2.3}$$

We make the usual assumption [1] that the growth rate G is inversely proportional to the amount of particulate surface area; that is,

$$G(n) = \frac{k_1}{\int_0^\infty R^2 n(R, \tau)\, dR}. \tag{2.4}$$

Furthermore, we exclude the possibility that particles of nonzero size are spontaneously produced. (This implies, for example, that particle breakage is excluded.) Then,

$$B(R, \tau) = 0 \quad \text{for } R \neq 0. \tag{2.5}$$

The simplest death rate $D(R, \tau)$ corresponds to removing particles indiscriminately from the container (i.e., mixed product removal). We assume that we have this mixed product removal in the form

$$D(R, \tau) = k_2 n(R, \tau). \tag{2.6}$$

Upon substituting (2.4), (2.5) and (2.6) into (2.3), we obtain

$$\frac{\partial n}{\partial \tau} + \frac{k_1}{\int_0^\infty R^2 n(R, \tau)\, dR} \frac{\partial n}{\partial x} + k_2 n = 0. \tag{2.7}$$

This is known as the crystallization equation.

We now need appropriate initial and boundary conditions for (2.7). It is generally assumed that

$$n(0, \tau) = \frac{k_3}{(\int_0^\infty R^2 n(R, \tau)\, dR)^p}, \qquad p > 0. \tag{2.8}$$

That is, the number of particles of zero size (nucleation) is inversely proportional to the total surface area of particles. Hence, the less surface area available for particle growth, the larger will be the number of particles forming at zero size. Our formulation is completed with the specification of a given initial distribution; that is,

$$n(R, 0) = F(R). \tag{2.9}$$

We must solve (2.7) subject to the conditions (2.8) and (2.9).

The problem (2.7)–(2.9) is one of the simplest in the theory of particulate formation. The more difficult problems arise from eliminating some of our simplifying assumptions. For example, R itself may be an n-dimensional vector, the components of which could be particle size, particle age, chemical composition, energy content, chemical activity, etc. Thus, R is a measure of the state of the particle. Furthermore, in most actual industrial situations one tries to remove only particles within a given size range; this implies a death rate $D(R, \tau)$ considerably more complex than that given by (2.6). Finally, we have ignored variations in the concentration of the solute. We shall not treat any of these added complexities here.

It will be convenient to introduce the following dimensionless variables:

$$\begin{aligned} t &= k_2 \tau, \qquad x = R\left[2k_3\left(\frac{k_2}{k_1}\right)^{p+1}\right]^{1/(p+4)}, \\ y(x, t) &= \left[\frac{2^p}{k_3^4}\left(\frac{k_1}{k_2}\right)^{3p}\right]^{1/(p+1)} n(R, \tau). \end{aligned} \tag{2.10}$$

Equations (2.7)–(2.9) then become

$$\frac{\partial y}{\partial t} + \frac{1}{\phi(t)} \frac{\partial y}{\partial x} + y = 0, \qquad x > 0, \quad t > 0, \tag{2.11}$$

$$y(0, t) = \frac{1}{\phi^p(t)}, \qquad t \geqq 0, \tag{2.12}$$

$$y(x, 0) = f(x), \qquad x \geqq 0, \tag{2.13}$$

where

$$\phi(t) = \frac{1}{2}\int_0^\infty x^2 y(x,t)\,dx, \tag{2.14}$$

and $f(x)$ represents arbitrarily prescribed initial data. We shall now analyze the system (2.11)–(2.14) involving the nonlinear integro-differential equation (2.11). Our interest will be primarily in oscillatory solutions for the distribution $y(x, t)$.

3. The moment equations. We shall see that the mechanism governing temporally periodic solutions of (2.11)–(2.14) is essentially the following: For small values of the parameter p, a stable steady state solution exists. As p is increased, this steady state loses its stability at some critical (or bifurcation) value $p = p^*$, and a stable periodic solution is set up. We shall establish this formally by asymptotic methods in $\delta = p - p^*$ for $0 < \delta \ll 1$.

By definition the kth moment $m_k(t)$ of the distribution $y(x, t)$ is given by

$$m_k(t) = \frac{1}{k!}\int_0^\infty x^k y(x,t)\,dx. \tag{3.1}$$

Hence, the $\phi(t)$ in our problem (2.11)–(2.14) is the second moment of $y(x, t)$. We shall see that we can obtain a closed system of nonlinear ordinary differential equations for the first three moments $m_k(t)$, $k = 1, 2, 3$. These will be solved asymptotically in δ. Thus, for small δ, $\phi(t)$ will be known, and (2.11)–(2.14) will reduce to a problem in linear first order partial differential equations with variable coefficients. We proceed now to implement these ideas.

Multiply (2.11) by x^k, integrate with respect to x from 0 to ∞, and assume that $y(x, t) \to 0$ as $x \to \infty$, to obtain

$$\frac{dm_k}{dt} + m_k - \frac{m_{k-1}}{m_2} = 0, \qquad k = 1, 2, \cdots. \tag{3.2}$$

Furthermore, integration of (2.11) with respect to x from 0 to ∞ yields

$$\frac{dm_0}{dt} + m_0 - \frac{1}{m_2^{p+1}} = 0. \tag{3.3}$$

Note that the equations for m_0, m_1 and m_2 form a closed system of three nonlinear ordinary differential equations. We now confine our attention to this system; that is, we study

$$\frac{dm_0}{dt} + m_0 - \frac{1}{m_2^{p+1}} = 0, \tag{3.4}$$

$$\frac{dm_1}{dt} + m_1 - \frac{m_0}{m_2} = 0, \tag{3.5}$$

$$\frac{dm_2}{dt} + m_2 - \frac{m_1}{m_2} = 0. \tag{3.6}$$

It is easy to show that the unique steady (i.e., $\partial/\partial t \equiv 0$) state solution of (2.11)–(2.14) is $y(x) = e^{-x}$. To analyze the stability of this steady state, note that for $y(x) = e^{-x}$ we have $m_k = 1$ for $k = 1, 2, 3$. Thus, the steady state corresponds to the critical point $(m_1, m_2, m_3) = (1, 1, 1)$ of the system (3.4)–(3.6). Upon linearizing (3.4)–(3.6) about this critical point, we find that the linearized system possesses only exponentially decaying solutions for $p < 20$ and exponentially growing solutions for $p > 20$. (For $p = 20$ the pair of complex eigenvalues have zero real part.) Therefore, the steady state is stable for $p < 20$ and unstable for $p > 20$, and the value $p = p^* = 20$ is the critical (or bifurcation) value at which we shall look for the appearance of time-dependent oscillatory solutions.

4. Periodic solutions of the moment equations. The linearized stability analysis of § 3 implies that for $p > p^* = 20$ perturbations from the steady state will initially grow exponentially in time. This (linearized) exponentially growing function cannot represent the solution for very long because clearly the nonlinear terms must then become important. If, in fact, this exponentially growing function tends to a stable oscillatory solution, as we suspect, then growth on another time scale must come into play so that in some sense the perturbation from the unstable steady state should exhibit a more or less typical multi-time scale representation; namely, we expect a representation of the form $m_k(t) = A_k(\tau)P_k(t^*)$, $k = 1, 2, 3$, where $P_k(t^*)$ represents a periodic oscillation on a so-called "fast time" t^* and $A_k(\tau)$ represents "slow time" modulation which perhaps approaches a constant value as $t \to \infty$. We shall now apply a multi-time scale (or "two-timing") perturbation technique in this way. Our method will produce a representation of the solution which is easily interpretable physically and from which the stability of the solution is immediately resolved without recourse to further analysis. Change of stability and the time evolution of the solution in somewhat different problems have been studied in this way by D. S. Cohen [2] and B. J. Matkowsky [3].

We shall now investigate the bifurcation of periodic solutions in the system

$$\frac{dX}{dt} = PX + \varepsilon^2 AX + g(X), \tag{4.1}$$

where

$$X = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad P = \begin{pmatrix} 0 & \beta & 0 \\ -\beta & 0 & 0 \\ 0 & 0 & -\mu \end{pmatrix}, \quad g(X) = \begin{pmatrix} g_1(x, y, z) \\ g_2(x, y, z) \\ g_3(x, y, z) \end{pmatrix}. \tag{4.2}$$

(The transformations which reduce the system (3.4)–(3.6) to the form (4.1) will be explicitly demonstrated in § 5.) Here $0 < \varepsilon \ll 1$, β and μ are constants, $A = (a_{ij})$ is a constant matrix, and the nonlinear functions $g_i(x, y, z)$, $i = 1, 2, 3$, contain no linear terms in x, y or z near $(x, y, z) = (0, 0, 0)$; that is,

$$g_i(0,0,0) = g_{ix}(0,0,0) = g_{iy}(0,0,0) = g_{iz}(0,0,0) = 0, \qquad i = 1, 2, 3. \tag{4.3}$$

The only necessary tool we shall need in carrying out the two-timing formalism is an elementary fact which we shall state in the form of an easily referenced lemma.

LEMMA. *The general solution of*

$$\frac{du}{dt} + v = m \sin t + n \cos t,$$

$$\frac{dv}{dt} - u = p \sin t + q \cos t$$

is

$$u(t) = A \sin t + B \cos t + \left(\frac{m-q}{2}\right) t \sin t + \left(\frac{n+p}{2}\right) t \cos t + \left(\frac{n-q}{2}\right) \sin t,$$

$$v(t) = -A \cos t + B \sin t + \left(\frac{n+p}{2}\right) t \sin t - \left(\frac{m-q}{2}\right) t \cos t + \left(\frac{m+q}{2}\right) \sin t.$$

Thus, in order to suppress secular terms (i.e., in order to have solutions bounded for all $t \geqq 0$*) it is sufficient to require* $m - q = 0$ *and* $n + p = 0$.

Now, we assume that

$$x = x(t^*, \tau) = \varepsilon x_1(t^*, \tau) + \varepsilon^2 x_2(t^*, \tau) + \cdots, \tag{4.4}$$

$$y = y(t^*, \tau) = \varepsilon y_1(t^*, \tau) + \varepsilon^2 y_2(t^*, \tau) + \cdots, \tag{4.5}$$

$$z = z(t^*, \tau) = \varepsilon z_1(t^*, \tau) + \varepsilon^2 z_2(t^*, \tau) + \cdots, \tag{4.6}$$

or equivalently,

$$X = X(t^*, \tau) = \sum_{n=1}^{\infty} \varepsilon^n X_n(t^*, \tau), \qquad \text{where } X_n = \begin{pmatrix} x_n \\ y_n \\ z_n \end{pmatrix}, \tag{4.7}$$

and where the "slow time" τ and the "fast time" t^* are defined by

$$\tau = \varepsilon^2 t, \tag{4.8}$$

$$t^* = (1 + \varepsilon\omega_1 + \varepsilon^2\omega_2 + \cdots)t. \tag{4.9}$$

We shall now require that the ω_i and the other unknowns which will occur shall be chosen according to the principle that we suppress secular terms in such a way that we generate a self-consistent procedure for determining bounded functions $X_i(t^*, \tau)$ with modulation only on the slow time scale. We shall now carry out this procedure.

With the definitions (4.8) and (4.9), we find that $d/dt = (1 + \varepsilon\omega_1 + \varepsilon^2\omega_2 + \cdots)(\partial/\partial t^*) + \varepsilon^2(\partial/\partial\tau)$. Thus, upon substituting (4.4)–(4.9) into (4.1) and equating coefficients of like powers of ε, we obtain

$$\frac{\partial X_1}{\partial t^*} = PX_1, \tag{4.10}$$

$$\frac{\partial X_2}{\partial t^*} - PX_2 = -\omega_1 \frac{\partial X_1}{\partial t^*} + G(X_1), \tag{4.11}$$

$$\frac{\partial X_3}{\partial t^*} - PX_3 = AX_1 - \omega_2 \frac{\partial X_1}{\partial t^*} - \omega_1 \frac{\partial X_2}{\partial t^*} + F(X_1, X_2), \tag{4.12}$$

where $G(X_1)$ and $F(X_1, X_2)$ represent higher order terms for which the precise formulas will be given later in equations (4.14) and (4.19), (4.20). The solution of (4.10) is

$$
\begin{aligned}
x_1(t^*, \tau) &= A(\tau)\sin\beta t^* + B(\tau)\cos\beta t^*, \\
y_1(t^*, \tau) &= A(\tau)\cos\beta t^* - B(\tau)\sin\beta t^*, \\
z_1(t^*, \tau) &= C(\tau)\, e^{-\mu t^*},
\end{aligned} \tag{4.13}
$$

where the unknowns $A(\tau)$, $B(\tau)$ and $C(\tau)$ will be determined at a later stage of the perturbation procedure. Using (4.13), we find that

$$
\begin{aligned}
G_i(X_1) = {} & \tfrac{1}{4}(A^2 + B^2)[g_{ixx}(0) + g_{iyy}(0)] \\
& + [\tfrac{1}{4}(A^2 - B^2)(g_{iyy}(0) - g_{ixx}(0)) + ABg_{ixy}(0)]\cos 2\beta t^* \\
& + [\tfrac{1}{2}(A^2 - B^2)g_{ixy}(0) + \tfrac{1}{2}AB(g_{ixx}(0) - g_{iyy}(0))]\sin 2\beta t^* \\
& + (\text{terms involving } e^{-\mu t^*} \text{ as a factor}), \qquad i = 1, 2, 3.
\end{aligned} \tag{4.14}
$$

We shall be interested in finding only the leading term of (4.7), and thus, we do not need to retain the exponentially decaying terms in (4.16) since these terms can never give rise to secular terms in the calculation of $A(\tau)$ and $B(\tau)$. Using our lemma to suppress secular terms in (4.11), we see immediately that we must require that $\omega_1 = 0$. Then, the solution of (4.11) is found to be

$$
\begin{aligned}
x_2(t^*, \tau) = {} & a\sin 2\beta t^* + b\cos 2\beta t^* + \frac{1}{4\beta}[g_{2xx}(0) + g_{2yy}(0)](A^2 + B^2) \\
& + D(\tau)\sin\beta t^* + E(\tau)\cos\beta t^* + (\text{terms in } e^{-\mu t^*}),
\end{aligned} \tag{4.15}
$$

$$
\begin{aligned}
y_2(t^*, \tau) = {} & c\sin 2\beta t^* + d\cos 2\beta t^* - \frac{1}{4\beta}[g_{1xx}(0) + g_{1yy}(0)](A^2 + B^2) \\
& + D(\tau)\cos\beta t^* - E(\tau)\sin\beta t^* + (\text{terms in } e^{-\mu t^*}),
\end{aligned} \tag{4.16}
$$

$$
\begin{aligned}
z_2(t^*, \tau) = {} & \frac{e}{\mu^2 + 4\beta^2}\sin 2\beta t^* + \frac{f}{\mu^2 + 4\beta^2}\cos 2\beta t^* \\
& + \frac{1}{4\mu}[g_{3xx}(0) + g_{3yy}(0)](A^2 + B^2) + (\text{terms in } e^{-\mu t^*}),
\end{aligned} \tag{4.17}
$$

where

$$
\begin{aligned}
a &= \frac{1}{3\beta}[\tfrac{1}{2}(A^2 + B^2)(g_{1yy}(0) - g_{1xx}(0) - g_{2xy}(0)) \\
&\qquad + AB(2g_{1xy}(0) - \tfrac{1}{2}g_{2xx}(0) + \tfrac{1}{2}g_{2yy}(0))], \\
b &= \frac{-1}{3\beta}[\tfrac{1}{4}(A^2 - B^2)(g_{2yy}(0) - g_{2xx}(0) + 4g_{1xy}(0)) \\
&\qquad + AB(g_{1xx}(0) - g_{1yy}(0) + g_{2xy}(0))], \\
c &= \frac{1}{3\beta}[\tfrac{1}{2}(A^2 - B^2)(g_{2yy}(0) - g_{2xx}(0) + g_{1xy}(0)) \\
&\qquad + AB(2g_{2xy}(0) + \tfrac{1}{2}g_{1xx}(0) - \tfrac{1}{2}g_{1yy}(0))],
\end{aligned}
$$

$$d = \frac{1}{3\beta}\left[\tfrac{1}{4}(A^2 - B^2)(g_{1yy}(0) - g_{1xx}(0) - 4g_{2xy}(0)) + AB(g_{1xy}(0) - g_{2xx}(0) + g_{2yy}(0))\right], \tag{4.18}$$

$$e = \tfrac{1}{2}(A^2 - B^2)(\mu g_{3xy}(0) + \beta g_{3yy}(0) - \beta g_{3xx}(0)) + \tfrac{1}{2}AB(\mu g_{3xx}(0) - \mu g_{3yy}(0) + 4\beta g_{3xy}(0)),$$

$$f = \tfrac{1}{4}(A^2 - B^2)(\mu g_{3yy}(0) - \mu g_{3xx}(0) - 4g_{3xy}(0)) + AB(\mu g_{3xy}(0) - \beta g_{3xx}(0) + \beta g_{3yy}(0)),$$

and where $D(\tau)$ and $E(\tau)$ must be determined at a later stage. Upon substituting (4.13)–(4.18) into (4.12), we find, after a considerable amount of algebraic and trigonometric manipulation, that the first two equations of (4.12) become

$$\begin{aligned}\frac{\partial x_3}{\partial t^*} - \beta y_3 = {} & \left[a_{11}A - a_{12}B - \frac{dA}{d\tau} + \omega_2\beta B + A(A^2 + B^2)(L_1 + P_1) + B(A^2 + B^2)(M_1 - Q_1)\right]\sin\beta t^* \\ & + \left[a_{11}B + a_{12}A - \frac{dB}{d\tau} - \omega_2\beta A + A(A^2 + B^2)(Q_1 - M_1) + B(A^2 + B^2)(L_1 + P_1)\right]\cos\beta t^* \\ & + (\text{terms in } e^{-\mu t^*} \text{ and higher harmonics}),\end{aligned} \tag{4.19}$$

$$\begin{aligned}\frac{\partial y_3}{\partial t^*} + \beta x_3 = {} & \left[a_{21}A - a_{22}B + \frac{dB}{d\tau} + \omega_2\beta A + A(A^2 + B^2)(L_2 + P_2) + B(A^2 + B^2)(M_2 - Q_2)\right]\sin\beta t^* \\ & + \left[a_{21}B + a_{22}A - \frac{dA}{d\tau} + \omega_2\beta B + A(A^2 + B^2)(Q_2 - M_2) + B(A^2 + B^2)(L_2 + P_2)\right]\cos\beta t^* \\ & + (\text{terms in } e^{-\mu t^*} \text{ and higher harmonics}),\end{aligned} \tag{4.20}$$

where, for $i = 1, 2$,

$$\begin{aligned}L_i = {} & \frac{1}{6\beta}g_{ixx}(0)\left[\frac{7}{4}g_{2yy}(0) + \frac{5}{4}g_{2xx}(0) + g_{1xy}(0)\right] \\ & + \frac{1}{12\beta}g_{iyy}(0)[g_{2yy}(0) - g_{2xx}(0) + g_{1xy}(0)] \\ & - \frac{1}{12\beta}g_{ixy}(0)\left[\frac{11}{2}g_{1xx}(0) + \frac{13}{2}g_{1yy}(0) + g_{2xy}(0)\right] \\ & + \frac{1}{4}g_{ixy}(0)[g_{3xx}(0) + g_{3yy}(0)],\end{aligned}$$

$$M_i = \frac{1}{12\beta} g_{ixx}(0)[g_{1xx}(0) - g_{1yy}(0) + g_{2xy}(0)]$$
$$+ \frac{1}{6\beta} g_{iyy}(0)\left[\frac{7}{4} g_{1xx}(0) + \frac{5}{4} g_{1yy}(0) + g_{2xy}(0)\right]$$
$$+ \frac{1}{12} g_{ixy}(0)\left[\frac{-5}{2} g_{2xx}(0) - \frac{7}{2} g_{2yy}(0) + g_{1xy}(0)\right]$$
$$+ \frac{1}{4(\mu^2 + 4\beta^2)} g_{ixy}(0)[\beta g_{3xx}(0) - \beta g_{3yy}(0) - \mu g_{3xy}(0)]$$
$$- \frac{1}{4\mu} g_{iyz}(0)[g_{3xx}(0) + g_{3yy}(0)] + \frac{1}{2(\mu^2 + 4\beta^2)} g_{iyz}(0)$$
$$\cdot \left[\frac{1}{4}\mu g_{3xx}(0) - \frac{1}{2}\mu g_{3yy}(0) + \beta g_{3xy}(0)\right],$$
$$P_i = \tfrac{1}{8}[g_{ixxx}(0) + g_{ixyy}(0)],$$
$$Q_i = \tfrac{1}{8}[g_{ixxy}(0) + g_{iyyy}(0)].$$

Now, the application of our lemma to the system (4.19), (4.20) implies that to suppress secular terms we must require that

$$(4.21)\quad \begin{aligned} 2\frac{dA}{d\tau} &= (a_{11} + a_{22})A + (a_{21} - a_{12})B + 2\omega_2\beta B \\ &\quad + A(A^2 + B^2)(L_1 + P_1 + Q_2 - M_2) \\ &\quad + B(A^2 + B^2)(L_2 + P_2 + M_1 - Q_1), \end{aligned}$$

$$(4.22)\quad \begin{aligned} 2\frac{dB}{d\tau} &= (a_{12} - a_{21})A + (a_{11} + a_{22})B - 2\omega_2\beta A \\ &\quad - A(A^2 + B^2)(L_2 + P_2 - Q_1 + M_1) \\ &\quad + B(A^2 + B^2)(L_1 + P_1 - M_2 + Q_2). \end{aligned}$$

The periodic nature of the solutions of $x_1(t^*, \tau)$ and $y_1(t^*, \tau)$ can now be established by employing a device due to J. D. Cole [4]. Multiply (4.21) by A and (4.22) by B, and then add the equations to obtain

$$(4.23)\quad \frac{dR}{d\tau} = \alpha R - \gamma R^2,$$

where

$$(4.24)\quad R = A^2 + B^2, \quad \alpha = a_{11} + a_{22}, \quad \gamma = M_2 - Q_2 - P_1 - L_1.$$

The solution of (4.23) is easily found to be

$$(4.25)\quad R(\tau) = \frac{\alpha}{\gamma} \frac{1}{1 + k e^{-\alpha\tau}},$$

where k is a constant. Thus, when $\alpha > 0$ (and $\gamma > 0$), equations (4.13) and (4.25) show that the solution $X_1(t^*, \tau)$ approaches a limit cycle in the x_1, y_1-plane of amplitude

$$\left(\frac{\alpha}{\gamma}\right)^{1/2}\varepsilon = \left(\frac{a_{11} + a_{22}}{M_2 - Q_2 - P_1 - L_1}\right)^{1/2}\varepsilon.$$

On the other hand, if $\alpha < 0$ (and $\gamma > 0$), the oscillatory solution decays to zero as $\tau \to \infty$. (The solution with $\gamma < 0$ is not of interest here.)

Our procedures have been entirely formal. A mathematically rigorous justification of these results is possible, however. Such a justification of this two-timing result is the content of the paper of J. P. Keener [5].

5. Periodic solutions of the crystallization equations. As stated in § 3 for $p < p^* = 20$, there exists a unique, stable, steady state solution of (2.11)–(2.14), and presumably for $p < 20$ for all initial data (2.13) the solution of the time-dependent problem (2.11)–(2.14) approaches this steady state solution as $t \to \infty$. We shall now show that for p slightly greater than $p^* = 20$ the solutions of (2.11)–(2.14), for arbitrary initial data, approach a limit cycle as $t \to \infty$.

Suppose, first, that $\phi(t)$ is a known positive function. Then, equations (2.11)–(2.13) reduce to a simple problem in linear first order partial differential equations which we can solve by using the method of characteristics. We find that

$$(5.1)\qquad y(x,t) = \begin{cases} f(x)\,e^{-t} & \text{if } x > \displaystyle\int_0^t \frac{dt}{\phi(t)}, \\[2ex] \dfrac{1}{[\phi(t_0)]^p}\,e^{-(t-t_0)}, & \text{where } x = \displaystyle\int_{t_0}^t \frac{dt}{\phi(t)}, \quad \text{if } x < \displaystyle\int_0^t \frac{dt}{\phi(t)}. \end{cases}$$

Note that since (by assumption at this stage) $\phi(t) > 0$, the characteristics are monotone and nonintersecting. Furthermore, if $\phi(t)$ is periodic with period T, then for any fixed x (with $x < \int_0^t dt/\phi(t)$) we have

$$\begin{aligned} y(x,t) &= \frac{e^{-(t-t_0)}}{[\phi(t_0)]^p}, & x &= \int_{t_0}^t \frac{dt}{\phi(t)}, \\ &= \frac{e^{-(t-T-[t_0+T])}}{[\phi(t_0+T)]^p}, & x &= \int_{t_0}^t \frac{dt}{\phi(t)} = \int_{t_0+T}^{t+T} \frac{dt}{\phi(t)}, \\ &= \frac{e^{-(t+T-t_1)}}{[\phi(t_1)]^p}, & x &= \int_{t_1}^{t+T} \frac{dt}{\phi(t)}, \\ &= y(x, t+T). \end{aligned}$$

Thus, for t sufficiently large (i.e., $x < \int_0^t dt/\phi(t)$), the solution, for fixed x, is periodic in t with period T. Furthermore, if, as $t \to \infty$, $\phi(t)$ approaches a periodic function of period T, then the solution $y(x, t)$ also approaches a periodic function of period T as $t \to \infty$ for fixed x.

We shall now show that $\phi(t)$ is, in fact, a known positive function which does approach a periodic function as $t \to \infty$. Furthermore, the virtue of our two-timing method yields (for sufficiently small ε) the entire time history of $\phi(t)$ and its manner of approach to a limit cycle. Thus, we can obtain the same time evolution for $y(x, t)$.

Once again consider the moment equations (3.4)–(3.6), and recall that $\phi(t) \equiv m_2(t)$. Let $p = 20 + 11\varepsilon^2$, and let $m_0 = 1 + u, m_1 = 1 + v$ and $m_2 = 1 + w$. Then, (3.4)–(3.6) become

$$\frac{du}{dt} = -u + \frac{1}{(1 + w)^{21 + 11\varepsilon^2}} - 1, \tag{5.2}$$

$$\frac{dv}{dt} = -v + \frac{1 + u}{1 + w} - 1, \tag{5.3}$$

$$\frac{dw}{dt} = -w + \frac{1 + v}{1 + w} - 1. \tag{5.4}$$

To put this system into the form considered in § 4, expand the right-hand sides of (5.2)–(5.4) in a Taylor series about $(u, v, w) = (0, 0, 0)$ and retain terms up to and including third order to obtain

$$\frac{du}{dt} = -u - (21 + 11\varepsilon^2)w + 231w^2 - 1771w^3, \tag{5.5}$$

$$\frac{dv}{dt} = u - v - w + w^2 - uw + uw^2 - w^3, \tag{5.6}$$

$$\frac{dw}{dt} = -v - 2w + w^2 - vw + vw^2 - w^3. \tag{5.7}$$

Now, make the transformation

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} -6\sqrt{3} & -3\sqrt{2} & 7 \\ -2\sqrt{3} & 2\sqrt{2} & -2 \\ 0 & \sqrt{2} & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \equiv T \begin{pmatrix} x \\ y \\ z \end{pmatrix},$$

so that

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \frac{1}{132} \begin{pmatrix} -4\sqrt{3} & -10\sqrt{3} & 8\sqrt{3} \\ -3\sqrt{2} & 9\sqrt{2} & 39\sqrt{2} \\ 6 & -18 & 54 \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix} = T^{-1} \begin{pmatrix} u \\ v \\ w \end{pmatrix}.$$

Under this transformation, the equations (5.5)–(5.7) become

$$\frac{d}{dt}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 & \beta(1 + \frac{1}{3}\varepsilon^2) & \frac{1}{3}\sqrt{3}\,\varepsilon^2 \\ -\beta & \frac{1}{2}\varepsilon^2 & \frac{1}{4}\sqrt{2}\,\varepsilon^2 \\ 0 & -\frac{1}{4}\sqrt{2}\,\varepsilon^2 & -\mu - \frac{1}{2}\varepsilon^2 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} g_1(x, y, z) \\ g_2(x, y, z) \\ g_3(x, y, z) \end{pmatrix}, \tag{5.8}$$

where $\beta = \sqrt{6}$, $\mu = -4$ and

$$g_1(x, y, z) = \frac{-162\sqrt{3}}{11}y^2 - \frac{151\sqrt{6}}{11}yz - \frac{70}{11}z^2 - \sqrt{2}\,xy$$

$$- xz + 2xy^2 + \frac{3566\sqrt{6}}{33}y^3,$$

$$g_2(x, y, z) = \frac{-116\sqrt{2}}{11}y^2 - \frac{221}{11}yz - \frac{105\sqrt{2}}{22}z^2 + 2\sqrt{3}\,xy$$

$$+ \sqrt{6}\,xz - 2\sqrt{6}\,xy^2 + \frac{1772}{11}y^3,$$

$$g_3(x, y, z) = \frac{210}{11}y^2 + \frac{243\sqrt{2}}{11}yz + \frac{138}{11}z^2 - \frac{1750\sqrt{2}}{11}y^3.$$

Therefore, (5.8) is precisely of the form of (4.1), and we may now apply all our results of § 4. For the system (5.8) we find that

$$L_1 = \frac{3137}{132}, \quad M_2 = \frac{25163}{132}, \quad P_1 = \frac{1}{2}, \quad Q_2 = \frac{1329}{11},$$

so that

$$\gamma = M_2 - Q_2 - P_1 - L_1 = \frac{501}{11} > 0.$$

Hence, we conclude that the system (5.2)–(5.4) possesses oscillatory solutions (limit cycles) and that all (sufficiently small) initial conditions lead to solutions which approach this limit cycle as $t \to \infty$. Thus, in particular, $w(t)$ is known, which implies that $\phi(t) \equiv m_2(t) = 1 + w(t)$ is known, which implies that (2.11)–(2.14) can be analyzed as a linear first order partial differential equation as we did in the first part of this section.

REFERENCES

[1] A. D. Randolph and M. A. Larson, *Theory of Particulate Processes*, Academic Press, New York, 1971.

[2] D. S. Cohen, *Multiple solutions and periodic oscillations in nonlinear diffusion processes*, this Journal, 25 (1974), pp. 640–654.

[3] B. J. Matkowsky, *A simple nonlinear dynamic stability problem*, Bull. Amer. Math. Soc., 76 (1970), pp. 620–625.

[4] J. D. Cole, *Perturbation Methods in Applied Mathematics*, Blaisdell, Waltham, Mass., 1968.

[5] J. P. Keener, *The long time validity of multiple scale expansions*, to appear.