Bifurcation Analysis of Polymerization Fronts

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A free boundary model is used to describe frontal polymerization. Weakly nonlinear analysis is applied to investigate pulsating instabilities in two dimensions. The analysis produces a pair of Landau equations, which describe the evolution of the linearly unstable modes. Onset and stability of spinning and standing modes is described.

Introduction

We consider the nonlinear dynamics of a free radical polymerization front in two dimensions. Frontal polymerization (FP) refers to the process, by which conversion from monomer to polymer occurs in a narrow region that propagates in space. It was first documented experimentally by Chechilo, Khvilivitskii and Enikolopyan *(1)*. In the simplest case, a polymerization front can be generated in a test tube containing a mixture of monomer and initiator by supplying heat to one end of the tube. The heat subsequently decomposes the initiator into free radicals, which trigger the highly exothermic process of free-radical polymerization. The focus of our attention will be the self-sustaining wave which travels through the tube as polymer molecules are being formed. Uniformly propagating planar waves may become unstable as parameters vary resulting in interesting nonlinear behaviors *(2)*. To ensure the desired uniformity and quality of the resulting product, it is important to have a clear understanding of the stability of the propagating front. A complete linear stability analysis was first presented by Schult and Volpert *(3)*, and a one-dimensional nonlinear stability analysis was done later by Gross and Volpert *(4)*. Our paper extends this nonlinear analysis to two dimensions, which allows us to describe and analyze the spinning waves that have been observed experimentally and also standing waves.

Mathematical Model

Consider a cylindrical shell of circumference L, in which the reaction propagates longitudinally. In a fixed coordinate frame $(\widetilde{x}, y)$ the direction of motion of the front is $-\widetilde{x}$ where $-\infty < \widetilde{x} < \infty$ and $0 < y < L$. By introducing a moving coordinate system $x = \widetilde{x} - \varphi(y, t)$ where φ is the location of the reaction front at time t, we fix the front at $x = 0$. The dependent variables in our model are the temperature $T(x, y, t)$, monomer concentration $M(x, y, t)$, initiator concentration $I(x, y, t)$ and velocity of the propagating front $u(y, t) = -\partial\phi(y, t)/dt$. Under sharp-interface approximation *(3)*, *(5)*, we solve the reactionless equations

$$\frac{\partial T}{\partial t} - \varphi_t \frac{\partial T}{\partial x} = \kappa \nabla^2 T,$$

$$\frac{\partial M}{\partial t} - \varphi_t \frac{\partial M}{\partial x} = 0,$$

$$\frac{\partial J}{\partial t} - \varphi_t \frac{\partial J}{\partial x} = 0,$$

both ahead of and behind the front. Here $J = \sqrt{I}$, κ is the thermal diffusivity and ∇^2 the Laplacian for the moving coordinate system defined as

$$\nabla^2 = \frac{\partial^2}{\partial y^2} + \left(1 + \phi_y^2\right) \frac{\partial^2}{\partial x^2} - 2\phi_y \frac{\partial^2}{\partial x \partial y} - \phi_{yy} \frac{\partial}{\partial x}.$$

Boundary conditions far ahead of the front $(x \to -\infty)$ are $T \to T_0$, $M \to M_0$, $J \to J_0$, whereas far behind the front $(x \to \infty)$, $T_x \to 0$. We assume that for all $x > 0$, $J = 0$, as the initiator is completely consumed as the reaction front progresses. We assume periodic boundary conditions in y for both T and φ. The front conditions derived from sharp-interface analysis are *(3)*, *(5)*

$$[T] = 0,$$

$$\kappa [T_x] = \frac{q (M_0 - M_b) \varphi_t}{1 + \varphi_y^2},$$

$$\frac{\varphi_t^2}{1 + \varphi_y^2} = F(T_b) \equiv \frac{\kappa k_{01} R_g T_b^2}{q M_0 E_1} \exp(j_0 - \frac{E_1}{R_g T_b}) \left(\int_0^{j_0} \frac{e^\eta - 1}{\eta} d\eta\right)^{-1},$$

$$M_b = f(T_b) = M_0 \exp(-j_0), \quad j_0 = \frac{J_0 A_2}{A_1}.$$

The brackets denote a jump in a quantity across the front $[v] = v(x = 0^+) - v(x = 0^-)$, q is the heat released per unit concentration of monomer, T_b and

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M_b are the temperature and monomer concentration at the front respectively, $A_i = k_{0i} \exp\left(-E_i/R_g T_b\right)$ is the Arrhenius function for decomposition $(i = 1)$ and polymerization $(i = 2)$ reactions, with k_{0i} and E_i being the frequency factors and activation energies of both processes. The universal gas constant is denoted as R_g.

Basic Solution and Its Stability

The stationary solution in 1-D is

$$\widehat{T}(x) = \left\{ \begin{array}{l} T_0 + (\widehat{T}_b - T_0) \exp\left(\widehat{u}x/\kappa\right), \quad x < 0 \\ \widehat{T}_b, \quad x > 0 \end{array} \right. ,$$

$$\widehat{M}(x) = \left\{ \begin{array}{l} M_0, \quad x < 0 \\ \widehat{M}_b, \quad x > 0 \end{array} \right. , \qquad \widehat{J}(x) = \left\{ \begin{array}{l} J_0, \quad x < 0 \\ 0, \quad x > 0 \end{array} \right. ,$$

$$\widehat{\varphi}_t = -\widehat{u} > 0,$$

where

$$\widehat{T}_b = T_0 + q(M_0 - \widehat{M}_b), \quad \widehat{M}_b = f(\widehat{T}_b), \quad \widehat{u}^2 = F(\widehat{T}_b).$$

A detailed account of the linear stability analysis of this system can be found in *(3), (4)*. We use the following non-dimensional parameters in the analysis

$$z_1 = \frac{F'(\widehat{T}_b)(\widehat{T}_b - T_0)}{F(\widehat{T}_b)} \equiv 2(\widehat{T}_b - T_0)\frac{\partial \ln \widehat{u}}{\partial \widehat{T}_b}, \quad z_2 = \frac{F''(\widehat{T}_b)(\widehat{T}_b - T_0)^2}{2F(\widehat{T}_b)},$$

$$z_3 = \frac{F'''(\widehat{T}_b)(\widehat{T}_b - T_0)^3}{6F(\widehat{T}_b)}, \quad P_1 = qf'(\widehat{T}_b) \equiv q\frac{\partial \widehat{M}_b}{\partial \widehat{T}_b},$$

$$P_2 = \frac{1}{2}q(\widehat{T}_b - T_0)f''(\widehat{T}_b), \quad P_3 = \frac{1}{6}q(\widehat{T}_b - T_0)^2 f'''(\widehat{T}_b).$$

The resulting dispersion relation in non-dimensional form is *(4)*

$$4\Omega^3 + (1 + 4s^2 + 4z_1 - (z_1 - P_1)^2)\Omega^2 + z_1(1 + 4s^2 + P_1)\Omega + s^2 z_1^2 = 0.$$

Here $k = 2\pi j/L$, $j = 1, 2, \ldots$, $s = \kappa k/\widehat{u}$ is the non-dimensional wavenumber and $\Omega = \kappa\omega/\widehat{u}^2$ is the non-dimensional frequency of oscillation. Instability occurs when a pair of complex conjugate eigenvalues crosses the imaginary axis

as the parameters vary. At the stability boundary

$$z_{1cr} = 4 + 2P_1 - 4s^2 \left(1 + 4s^2 + P_1\right)^{-1}$$

$$+2\left(\left(2 + P_1 - 2s^2\left(1 + 4s^2 + P_1\right)^{-1}\right)^2 - P_1^2 + 1 + 4s^2\right)^{\frac{1}{2}},$$

$$\omega_0^2 = \left(\operatorname{Im}\Omega\right)^2 = \frac{1}{8}z_{1cr}\left(1 + 4s^2 + P_1\right).$$

The neutral stability curve in the (s, z_1) plane has a minimum at $s = s_m > 0$ for all $P_1 \geq 0$.

Weakly Nonlinear Analysis

We perform a nonlinear analysis that will allow us to obtain amplitude equations to characterize the evolution of the unstable modes. Gross and Volpert *(4)* have studied the 1-D case for loss of neutral stability at the wavenumber $s = 0$. This corresponds to sufficiently small values of the tube circumference L. The analysis in this instance results in a single Landau-Stuart equation which governs the weakly unstable modes. If, however, the tube circumference L is large, loss of stability will occur for some $s > 0$. Our nonlinear analysis yields a coupled set of Landau amplitude equations.

We introduce time scales $t_0 = t$, $t_1 = \epsilon t$, $t_2 = \epsilon^2 t$ and expand T, M, and φ as $T = \widehat{T} + \epsilon T_1 + \epsilon^2 T_2 + \epsilon^3 T_3 + ...$, $M = \widehat{M} + \epsilon M_1 + \epsilon^2 M_2 + \epsilon^3 M_3 + ...$, $\varphi = -\widehat{u}t_0 + \epsilon\varphi_1 + \epsilon^2\varphi_2 + \epsilon^3\varphi_3 + ...$ Also $z_1 = z_{1cr} + \mu\epsilon^2$. To non-dimensionalize the above the following scales are used , where $j = 0, 1, 2$

$$\xi = \frac{\widehat{u}}{\kappa}x, \quad \eta = \frac{\widehat{u}}{\kappa}y, \quad \psi = \frac{\widehat{u}}{\kappa}\varphi, \quad \psi_j = \frac{\widehat{u}}{\kappa}\varphi_j, \quad t_j = \frac{\kappa}{\widehat{u}^2}\tau_j, \quad \theta = \frac{T}{\widehat{T}_b - T_0},$$

$$\theta_b = \frac{T_b}{\widehat{T}_b - T_0}, \quad m = \frac{M}{-\widehat{M}_b + M_0}, \quad m_b = \frac{M_b}{-\widehat{M}_b + M_0}, \quad m_{jb} = \frac{M_{jb}}{-\widehat{M}_b + M_0}.$$

Consequently, we have the following sequence of problems

$$\frac{\partial\theta_j}{\partial\tau_0} + \frac{\partial\theta_j}{\partial\xi} - \left(\frac{\partial^2\theta_j}{\partial\xi^2} + \frac{\partial^2\theta_j}{\partial\eta^2}\right) - \left(\frac{\partial\psi_j}{\partial\tau_0} + \frac{\partial^2\psi_j}{\partial\eta^2}\right)\frac{d\widehat{\theta}}{d\xi} = \widetilde{Q}_j, \qquad (1)$$

$$[\theta_j] = 0, \quad \left[\frac{\partial\theta_j}{\partial\xi}\right] - \frac{\partial\psi_j}{\partial\tau_0} - m_{jb} = \widetilde{R}_j, \qquad (2)$$

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$$2\frac{\partial \psi_j}{\partial \tau_0} + z_{1cr}\theta_{jb} = \widetilde{S}_j, \quad m_{jb} - P_1\theta_{jb} = \widetilde{T}_j, \tag{3}$$

where $\widetilde{Q}_j$, $\widetilde{R}_j$, $\widetilde{S}_j$ and $\widetilde{T}_j$ are given in the Appendix. The solution θ_j, ψ_j satisfy periodic boundary conditions in η and

$$\left.\frac{\partial \theta_j}{\partial \xi}\right|_{\xi=+\infty} = 0, \quad \theta_j|_{\xi=-\infty} = 0, \tag{4}$$

where $\widetilde{Q}_j$, $\widetilde{R}_j$, $\widetilde{S}_j$ and $\widetilde{T}_j$ are given in the Appendix.

The solvability condition for problem (1)-(4) is

$$\int_0^{\frac{2\pi}{\omega_0}} \int_0^L \left(\overline{v}|_{\xi=0} \left(\frac{P_1}{z_{1cr}}\widetilde{S}_j + \widetilde{R}_j + \widetilde{T}_j \right) - \frac{1}{z_{1cr}}\widetilde{S}_j \left[\frac{\partial \overline{v}}{\partial \xi} \right] \right) d\eta \, d\tau_0$$
$$= \int_0^{\frac{2\pi}{\omega_0}} \int_0^L \int_{-\infty}^{\infty} \widetilde{Q}_j \overline{v} \, d\tau_0 \, d\eta \, d\xi,$$

where $\overline{v}$ is a solution of the adjoint problem

$$v_{\pm}(\xi,\eta,\tau_0) = \left\{ \begin{array}{l} \exp\left(i\omega_0\tau_0 \pm is\eta + \frac{1}{2}\left(-1+\overline{d}\right)\xi \right), \ \xi < 0 \\ \exp\left(i\omega_0\tau_0 \pm is\eta + \frac{1}{2}\left(-1-\overline{d}\right)\xi \right), \ \xi > 0 \end{array} \right. ,$$

$$v_0(\xi) = \left\{ \begin{array}{l} 1, \ \xi < 0 \\ \exp(-\xi), \ \xi > 0 \end{array} \right. .$$

The $O(\epsilon)$ Problem (j=1)

The solution of the $O(\epsilon)$ problem is

$$\theta_1 = \left(Ae^{i(\omega_0\tau_0+s\eta)} + Be^{i(\omega_0\tau_0-s\eta)} \right) X_1(\xi) + CC,$$
$$\psi_1 = \frac{Az_{1cr}}{2}e^{i(\omega_0\tau_0+s\eta)} + \frac{Bz_{1cr}}{2}e^{i(\omega_0\tau_0-s\eta)} + CC + \mho,$$

where CC denotes the complex conjugate, $\mho$, A and B are functions of the slow times and

$$X_1(\xi) = \left\{ \begin{array}{l} -\left(i\omega_0 + \frac{1}{2}z_{1cr} \right) e^{\frac{1}{2}(1+d)\xi} + \frac{1}{2}z_{1cr}e^{\xi}, \ \xi < 0 \\ -i\omega_0 e^{\frac{1}{2}(1-d)\xi}, \ \xi > 0 \end{array} \right. .$$

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The $O\left(\epsilon^2\right)$ Problem (j=2)

Applying the solvability condition to the $O\left(\epsilon^2\right)$ problem with $v = v_+$ and $v = v_-$ shows that A and B depend only on the slow time τ_2. When $v = v_0$ the solvability condition yields $\partial\mho/d\tau_1 = r_0\left(|A|^2 + |B|^2\right)$ with r_0 as

$$
r_0 = \frac{z_{1cr}}{-2(P_1 + 1)}\left\{-2\omega_0^2\left(\frac{P_1 + 1}{z_{1cr}}\left(\frac{1}{4}z_{1cr}^2 - z_2\right) + \frac{1}{2}z_{1cr}P_1 + P_2\right)\right.
$$

$$
-\frac{s^2 z_{1cr}^2}{2}\left(1 - \frac{P_1 + 1}{z_{1cr}}\right) - \frac{z_{1cr}\omega_0^2}{2}\left(2 + \frac{1 - \overline{d}}{1 + \overline{d}} + \frac{1 - d}{1 + d}\right)
$$

$$
\left.-\frac{s^2 z_{1cr}i\omega_0}{2}\left(\frac{1 - \overline{d}}{1 + \overline{d}} - \frac{1 - d}{1 + d}\right) + \frac{s^2}{2}z_{1cr}^2\right\}.
$$

The solution for the $O\left(\epsilon^2\right)$ problem is

$$
\theta_2 = g_0\left(\xi\right)\left(|A|^2 + |B|^2\right) + \{g_1\left(\xi\right)\left(A^2\exp(2i\left(\omega_0\tau_0 + s\eta\right))\right.
$$

$$
+ B^2\exp\left(2i\left(\omega_0\tau_0 - s\eta\right)\right))
$$

$$
+ g_2\left(\xi\right)AB\exp\left(2i\omega_0\tau_0\right) + g_3\left(\xi\right)A\overline{B}\exp\left(2is\eta\right) + CC\},
$$

$$
\psi_2 = C_0\left(|A|^2 + |B|^2\right) + \{C_1\left(A^2\exp\left(2i\left(\omega_0\tau_0 + s\eta\right)\right)\right.
$$

$$
+ B^2\exp\left(2i\left(\omega_0\tau_0 - s\eta\right)\right))
$$

$$
+ C_2 AB\exp\left(2i\omega_0\tau_0\right) + C_3 A\overline{B}\exp\left(2is\eta\right) + CC\},
$$

where the functions $g_j\left(\xi\right)$ are

$$
g_0 = \begin{cases} D_{01}\exp\left(\xi\right) + D_{02}\left(\exp\left(\xi\right) + \xi\exp\left(\xi\right)\right) \\ \quad + (D_{03}\exp((1 + d)\frac{\xi}{2}) + CC), \ \ \xi < 0 \\ a_{02} + (D_{04}\exp((1 - d)\frac{\xi}{2}) + CC), \ \ \xi > 0 \end{cases}
$$

$$
g_1 = \begin{cases} a_{11}\exp((1 + d_1)\frac{\xi}{2}) + D_{11}\exp(\xi) + D_{13}\exp((1 + d)\frac{\xi}{2}), \ \ \xi < 0, \\ \quad a_{12}\exp((1 - d_1)\frac{\xi}{2}) + D_{14}\exp((1 - d)\frac{\xi}{2}), \ \ \xi > 0 \end{cases}
$$

$$g_2 = \begin{cases} a_{21} \exp((1+d_2)\tfrac{\xi}{2}) + D_{21}\exp(\xi) + D_{23}\exp((1+d)\tfrac{\xi}{2}), & \xi < 0, \\ a_{22}\exp((1-d_2)\tfrac{\xi}{2}) + D_{24}\exp((1-d)\tfrac{\xi}{2}), & \xi > 0 \end{cases}$$

$$g_3 = \begin{cases} a_{31}\exp((1+d_3)\tfrac{\xi}{2}) + D_{31}\exp(\xi) \\ \quad + (D_{33}\exp((1+d)\tfrac{\xi}{2}) + CC), & \xi < 0, \\ a_{32}\exp((1-d_3)\tfrac{\xi}{2}) + (D_{34}\exp((1-d)\tfrac{\xi}{2}) + CC), & \xi > 0 \end{cases}$$

Here, $d_1 = \sqrt{1 + 8i\omega_0 + 16s^2}$, $d_2 = \sqrt{1 + 8i\omega_0}$ and $d_3 = \sqrt{1 + 16s^2}$ and the coefficients a_{ij}, D_{ij} and C_j are given in the Appendix.

The $O\left(\epsilon^3\right)$ Problem (j=3)

The solvability conditions for the $O\left(\epsilon^3\right)$ problem yield a coupled set of Landau equations

$$\frac{\partial A}{\partial \tau_2} = \mu A \chi + A^2 \overline{A} \beta_1 + AB\overline{B}\beta_2, \quad \frac{\partial B}{\partial \tau_2} = \mu B \chi + B^2 \overline{B} \beta_1 + AB\overline{A}\beta_2. \quad (5)$$

The complex coefficients β_1, β_2 and χ are given in the Appendix.

Analysis of the Amplitude Equations

We let the amplitudes A and B of ψ_1, which determines the shape of the front, be of the form

$$A\left(\tau_2\right) = a\left(\tau_2\right)\exp\left(i\theta_a \tau_2\right), \; B\left(\tau_2\right) = b\left(\tau_2\right)\exp\left(i\theta_b \tau_2\right). \quad (6)$$

Substituting (6) into (5) and separating real and imaginary parts results in

$$\frac{da}{d\tau_2} = \mu\chi_r a + \beta_{1r}a^3 + \beta_{2r}ab^2, \quad \frac{d\theta_a}{d\tau_2} = \mu\chi_i + \beta_{1i}a^2 + \beta_{2i}b^2, \quad (7)$$

$$\frac{db}{d\tau_2} = \mu\chi_r b + \beta_{1r}b^3 + \beta_{2r}a^2 b, \quad \frac{d\theta_b}{d\tau_2} = \mu\chi_i + \beta_{1i}b^2 + \beta_{2i}a^2. \quad (8)$$

Here the subscripts r and i represent the real and imaginary parts of the respective coefficients. In order to determine the steady state solutions of (7), (8) which, in the original problem, correspond to a superposition of waves traveling along the front, we consider $da/d\tau_2 = db/d\tau_2 = 0$. This leads to

$$a\left(\mu\chi_r + \beta_{1r}a^2 + \beta_{2r}b^2\right) = 0, \; b\left(\mu\chi_r + \beta_{1r}b^2 + \beta_{2r}a^2\right) = 0. \quad (9)$$

There are four critical points

$$a_1 = b_1 = 0, \quad a_2 = 0, \; b_2 = w_t, \quad a_3 = w_t, \; b_3 = 0, \quad a_4 = b_4 = w_s,$$

where

$$w_t = (-\mu \chi_r / \beta_{1r})^{1/2}, \quad w_s = (-\mu \chi_r / (\beta_{1r} + \beta_{2r}))^{1/2}.$$

In the case of the first critical point the amplitudes A and B are identically equal to zero, which corresponds to the uniformly propagating wave in the original problem. The second and third critical points correspond to waves traveling along the front, which are right- and left-traveling waves, respectively. The last critical point corresponds to a standing wave.
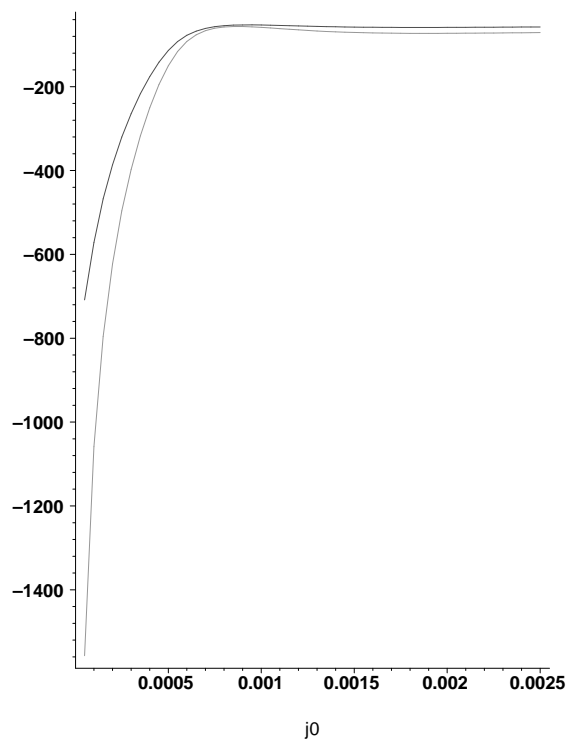

Figure 1. Graphs of β_{1r} (upper curve) and β_{2r} (lower curve) versus the non-dimensional $j_0 = J_0 \frac{A_2}{A_1}$

It can be shown that for all parameter values χ_r is positive. Thus, from the expression for w_t we conclude that left- and right-traveling wave exist for $\mu > 0$ (the

so-called supercritical bifurcation) if $\beta_{1r} < 0$ and for $\mu < 0$ (the subcritical bifurcation) if $\beta_{1r} > 0$. In a similar way, the supercritical bifurcation of standing waves occurs if $\beta_{1r} + \beta_{2r} < 0$ and subcritical bifurcation occurs if $\beta_{1r} + \beta_{2r} > 0$. All the subcritical bifurcations are known to produce locally unstable regimes. The supercritical bifurcation can lead to either stable or unstable solutions depending on the parameter values. Specifically, the supercritical bifurcation of traveling waves (which occurs if $\beta_{1r} < 0$) is stable if $\beta_{2r} < \beta_{1r}$ and unstable otherwise. The supercritical bifurcation of standing waves (which occurs if $\beta_{1r} + \beta_{2r} < 0$) is stable if $\beta_{2r} > \beta_{1r}$ and unstable otherwise.

The quantities β_{1r} and β_{2r} are plotted in Fig. 1 as functions of j_0 (which is proportional to the initial concentration of the initiator) for typical parameter values (3) $(E_1 - E_2)/(R_g q M_0) = 19.79$ and $E_1/(R_g q M_0) = 58.4$. We set the wavenumber $s = 0.55$, which is close to the value s_m at which the neutral stability curve has a minimum (4). We see that both quantities are negative, which implies that both traveling and standing waves appear as a result of a supercritical bifurcation, and that for the parameter values chosen $\beta_{1r} > \beta_{2r}$, so that the traveling waves are stable while the standing waves are unstable. This observation agrees with the experimental data in (2) where spinning waves have been observed.

Acknowledgements

Appendix

The right-hand side of equations (1)-(3) are

$$\widetilde{Q}_1 = 0, \quad \widetilde{Q}_2 = \frac{\partial}{\partial \tau_1}\left(\psi_1 \frac{d\widehat{\theta}}{d\xi} - \theta_1\right) + \left(\frac{\partial \psi_1}{\partial \tau_0} - \frac{\partial^2 \psi_1}{\partial \eta^2}\right)\frac{\partial \theta_1}{\partial \xi}$$

$$+ \frac{\partial \psi_1}{\partial \eta}\frac{\partial}{\partial \xi}\left(\frac{\partial \psi_1}{\partial \eta}\frac{d\widehat{\theta}}{d\xi} - 2\frac{\partial \theta_1}{\partial \eta}\right)$$

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$$\widetilde{Q}_3 = \left(\frac{\partial \psi_2}{\partial \tau_0} - \frac{\partial^2 \psi_2}{\partial \eta^2} \right) \frac{\partial \theta_1}{\partial \xi} + \frac{\partial}{\partial \tau_1} \left(\psi_2 \frac{d\widehat{\theta}}{d\xi} - \theta_2 \right) + \frac{\partial}{\partial \tau_2} \left(\psi_1 \frac{d\widehat{\theta}}{d\xi} - \theta_1 \right)$$

$$+ \frac{\partial \psi_1}{\partial \eta} \frac{\partial}{\partial \xi} \left(\frac{\partial \psi_1}{\partial \eta} \frac{\partial \theta_1}{\partial \xi} - 2 \frac{\partial \theta_2}{\partial \eta} \right) + \frac{\partial \psi_1}{\partial \tau_1} \frac{\partial \theta_1}{\partial \xi}$$

$$+ 2 \frac{\partial \psi_2}{\partial \eta} \frac{\partial}{\partial \eta} \left(\psi_1 \frac{d^2\widehat{\theta}}{d\xi^2} - \frac{\partial \theta_1}{\partial \xi} \right) + \left(\frac{\partial \psi_1}{\partial \tau_0} - \frac{\partial^2 \psi_1}{\partial \eta^2} \right) \frac{\partial \theta_2}{\partial \xi},$$

$$\widetilde{R}_1 = 0, \ \ \widetilde{R}_2 = \left(\frac{\partial \psi_1}{\partial \eta} \right)^2 + \frac{\partial \psi_1}{\partial \tau_1} - m_{1b} \frac{\partial \psi_1}{\partial \tau_0},$$

$$\widetilde{R}_3 = 2 \frac{\partial \psi_1}{\partial \eta} \frac{\partial \psi_2}{\partial \eta} - \frac{\partial \psi_1}{\partial \tau_0} \left(\frac{\partial \psi_1}{\partial \eta} \right)^2 + \frac{\partial \psi_2}{\partial \tau_1} + \frac{\partial \psi_1}{\partial \tau_2}$$

$$- m_{1b} \left(\left(\frac{\partial \psi_1}{\partial \eta} \right)^2 + \frac{\partial \psi_2}{\partial \tau_0} + \frac{\partial \psi_1}{\partial \tau_1} \right) - m_{2b} \frac{\partial \psi_1}{\partial \tau_0},$$

$$\widetilde{S}_1 = 0, \ \widetilde{S}_2 = -2 \frac{\partial \psi_1}{\partial \tau_1} - z_2 \left(\theta_{1b} \right)^2 - \left(\frac{\partial \psi_1}{\partial \eta} \right)^2 + \left(\frac{\partial \psi_1}{\partial \tau_0} \right)^2,$$

$$\widetilde{S}_3 = -2 \frac{\partial \psi_2}{\partial \tau_1} - 2 \frac{\partial \psi_1}{\partial \tau_2} + 2 \frac{\partial \psi_1}{\partial \tau_0} \left(\frac{\partial \psi_2}{\partial \tau_0} + \frac{\partial \psi_1}{\partial \tau_1} \right) - 2 z_2 \theta_{1b} \theta_{2b}$$

$$- z_3 \left(\theta_{1b} \right)^3 - \mu \theta_{1b} - z_{1cr} \theta_{1b} \left(\frac{\partial \psi_1}{\partial \eta} \right)^2 - 2 \frac{\partial \psi_1}{\partial \eta} \frac{\partial \psi_2}{\partial \eta},$$

$$\widetilde{T}_1 = 0, \ \ \widetilde{T}_2 = P_2 \left(\theta_{1b} \right)^2, \ \widetilde{T}_3 = 2 P_2 \theta_{1b} \theta_{2b} + P_3 \left(\theta_{1b} \right)^3.$$

The coefficients a_{ij}, D_{ij} and C_i appearing in the expressions for $g_i \left(\xi \right)$ are

$$D_{02} = -r_0, \ D_{03} = \left(s^2 + i\omega \right) z_{1cr} (i\omega_0 + z_{1cr}/2)(1 - d)^{-1},$$

$$D_{04} = z_{1cr} \left(s^2 + i\omega_0 \right) i\omega_0 (1 + d)^{-1},$$

$$D_{01} = -(1 + P_1)^{-1} \{ 2\omega_0^2 P_2 + s^2 z_{1cr}^2/2 + P_1 \omega^2 z_{1cr} - ((1 - d) D_{04}/2 + CC) + ((1 + d) D_{03}/2 + CC) + P_1 \left(D_{03} + CC \right) \},$$

$$a_{02} = D_{01} + D_{03} + \overline{D_{03}} - D_{04} - \overline{D_{04}}.$$

$$D_{13} = -(i\omega_0 + z_{1cr}/2)(1+d)\,z_{1cr}/4, \; D_{14} = -i\omega_0 z_{1cr}(1-d)/4,$$

$$\begin{aligned}
a_{12} = \{ &D_{14}((d+d_1)/2 + P_1) + D_{13}(d-d_1)/2 + z_{1cr}^2(1-d_1)/16 \\
&- \omega_0^2 P_2 - s^2 z_{1cr}^2/4 - P_1\omega_0^2 z_{1cr}/2 - (\omega_0^2 z_2 + s^2 z_{1cr}^2/4 \\
&- z_{1cr}^2\omega_0^2/4 - z_{1cr}D_{14})(4i\omega_0)^{-1}(0.5 - 0.5d_1 + 2i\omega_0)\}\{(1-d_1)/2 \\
&- (1 + z_{1cr}/4i\omega_0)(1+d_1)/2 + z_{1cr}/4i\omega_0 + z_{1cr}/2 - P_1\}^{-1}
\end{aligned}$$

$$C_1 = \{\omega_0^2 z_2 + s^2 z_{1cr}^2/4 - z_{1cr}^2\omega_0^2/4 - z_{1cr}a_{12} - z_{1cr}D_{14}\}(4i\omega_0)^{-1},$$

$$D_{11} = C_1 + z_{1cr}^2/8 \,,\; a_{11} = a_{12} + D_{14} - D_{11} - D_{13}.$$

$$D_{23} = -0.5z_{1cr}(1+d)(i\omega_0 + 0.5z_{1cr}) = 2D_{13},$$

$$D_{24} = -0.5z_{1cr}i\omega_0(1-d) = 2D_{14},$$

$$\begin{aligned}
a_{22} = \{ &0.5(d-d_2)D_{23} + D_{24}\{0.5(d+d_2) + P_1 - z_1(4i\omega_0)^{-1}(1 + 2i\omega_0 \\
&- 0.5(1+d_2))\} - z_{1cr}^2(d_2-1)/8 + 0.5s^2 z_{1cr}^2 - P_1 z_1\omega_0^2 - 2P_2\omega_0^2 \\
&+ (1 + 2i\omega_0 - (1+d_2)/2)(2\omega_0^2(z_2 - 0.25z_{1cr}^2) - 0.5s^2 z_{1cr}^2)(4i\omega_0)^{-1}\}/ \\
&\{-d_2 + z_{1cr}(1 + 2i\omega_0 - 0.5(1+d_2))/4i\omega_0 - P_1\}
\end{aligned}$$

$$C_2 = (-z_{1cr}a_{22} - z_{1cr}D_{24} - s^2 z_{1cr}^2/2 + 2\omega_0^2 z_2 - z_{1cr}^2\omega_0^2/2)/4i\omega_0,$$

$$D_{21} = C_2 + z_{1cr}^2/4, \; D_{33} = D_{13}, \; D_{34} = D_{14},$$

$$\begin{aligned}
a_{21} = \;&a_{22}(1 + z_{1cr}/4i\omega_0) + D_{24} - z_{1cr}^2/4 - D_{23} \\
&- (-z_{1cr}D_{24} - s^2 z_{1cr}^2/2 + 2\omega_0^2 z_2 - z_{1cr}^2\omega_0^2/2)/4i\omega_0.
\end{aligned}$$

$$a_{32} = s^2 z_{1cr}/2 - 2\omega_0^2 z_2/z_{1cr} + z_{1cr}\omega_0^2/2 - D_{34} - \overline{D_{34}},$$

$$\begin{aligned}
a_{31} = \{ &-a_{32}((d_3+1)/2 + P_1) - (D_{34}((d+1)/2 - P_1) + CC) \\
&+ (D_{33}(1-d)/2 + CC) + s^2 z_{1cr}^2/2 - 2\omega_0^2 P_2 - P_1\omega_0^2 z_{1cr}\}(d_3-1)/2,
\end{aligned}$$

$$C_3 = a_{32} - a_{31} - z_{1cr}^2/4 - D_{33} - \overline{D_{33}} + D_{34} + \overline{D_{34}}, \ D_{31} = C_3 + z_{1cr}^2/4.$$

The coefficients in the amplitude equations (5)) are

$$\chi = i\omega_0 \left(P_1 + d\right) \left\{z_{1cr}(P_1 + d - z_{1cr}/2 + 2i\omega_0/d + z_{1cr}/(2d))\right\}^{-1},$$

$$\beta_1 = (Q_5 - Q_1 - Q_3) \left\{P_1 + d - z_{1cr}/2 + 2i\omega_0/d + z_{1cr}/(2d)\right\}^{-1},$$

$$\beta_2 = (Q_6 - Q_2 - Q_4) \left\{P_1 + d - z_{1cr}/2 + 2i\omega_0/d + z_{1cr}/2d\right\}^{-1},$$

$$Q_1 + Q_3 = 2i\omega_0 C_1 I_3 + r_0 I_2 - 0.25 z_{1cr}^2 s^2 I_5 + 0.5 z_{1cr}^2 s^2 I_4 - 2 z_{1cr} s^2 I_7$$
$$+ 2 z_{1cr} s^2 C_1 I_1 + 0.5 z_{1cr}(i\omega_0 + s^2) I_6 + 0.5 z_{1cr}(-i\omega_0 + s^2) I_7,$$

$$Q_2 + Q_4 = 2i\omega_0 C_2 I_3 + r_0 I_2 + 0.5 z_{1cr}^2 s^2 I_5 - 2 z_{1cr} s^2 I_9 + 2 z_{1cr} s^2 C_3 I_1$$
$$+ 0.5 z_{1cr}(i\omega_0 + s^2)(I_6 + I_9) + 0.5 z_{1cr}(-i\omega_0 + s^2) I_7,$$

$$I_1 = 2/(1+d),$$

$$I_2 = -i\omega_0/d + 0.25 z_{1cr}(d-1)\{1/d - 2/(1+d)\},$$

$$I_3 = 2i\omega_0/(d+\overline{d}) + 0.5 z_{1cr}(d-1)\{1/(d+\overline{d}) - 1/(1+d)\},$$

$$I_4 = -0.5 i\omega_0(d+1/d) + 1/8 z_{1cr}(d-1)^3/\{d(d+1)\} - 0.25 z_{1cr}(d-1),$$

$$I_5 = i\omega_0(\overline{d} - d) + 0.25 z_{1cr}(1 - \overline{d}) + i\omega_0(d^2 + 1)/(d + \overline{d})$$
$$+ 0.25 z_{1cr}(d-1)^2\{1/(d+1) - 1/(d+\overline{d})\},$$

$$I_6 = -0.5(d-1)\{2D_{01}/(d+1) - 4D_{02}/(d+1)^2 + D_{03}/d + 2\overline{D_{03}}/(d+\overline{d})\}$$
$$+ 0.5(d+1)\{2a_{02}/(d+1) + D_{04}/d + 2\overline{D_{04}}/(d+\overline{d})\},$$

$$I_7 = -0.5(d-1)\{2a_{11}/(d+d_1) + 2D_{11}/(d+1) + D_{13}/d\}$$
$$+ 0.5(d+1)\{2a_{12}/(d+d_1) + D_{14}/d\},$$

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$$I_8 = -0.5(d-1)\{2a_{21}/(d+d_1) + 2D_{21}/(d+1) + D_{23}/d\}$$
$$+ 0.5(d+1)\{2a_{22}/(d+d_1) + D_{24}/d\},$$

$$I_9 = -0.5(d-1)\{2a_{31}/(d+d_3) + 2D_{31}/(d+1) + D_{33}/d + 2\overline{D_{33}}/(d+\overline{d})\}$$
$$+ 0.5(d+1)\{2a_{32}/(d+d_3) + D_{34}/d + 2\overline{D_{34}}/(d+\overline{d})\},$$

$$Q_5 = (P_1 + d)/z_{1cr}\{i\omega_0 z_{1cr} r_0 + 2i z_2 \omega_0 g_0(0) + 2\omega_0^2 z_{1cr} C_1$$
$$+ 3i\omega_0 z_{1cr}^3 s^2/4 - 2s^2 z_{1cr} C_1 + 3i z_3 \omega_0^3 - 2i z_2 \omega_0 g_1(0)\}$$
$$- i\{P_1\omega_0(-8r_0 + 4z_{1cr} g_0(0) - 4z_{1cr} g_1(0)$$
$$- 6s^2 z_{1cr}^2) + 16i C_1\left(P_1\omega_0^2 + s^2 z_{1cr}\right) + 3\omega_0 z_{1cr}\left(s^2 z_{1cr}^2 + 4\omega_0^2 P_2\right)\}/8$$
$$- 2i P_2 \omega_0 g_0(0) + 2i P_2 \omega_0 g_1(0) - 3i P_3 \omega_0^3,$$

$$Q_6 = (P_1 + d)/z_{1cr}\{2i\omega_0 z_2\left(g_3(0) - g_2(0) + g_0(0)\right) + 6i\omega_0^3 z_3$$
$$+ 2\omega_0^2 z_{1cr} C_2 + i\omega_0 z_{1cr} r_0 - 2s^2 z_{1cr} C_3 - i\omega_0 z_{1cr}^3 s^2/2\}$$
$$- i\{4\omega_0 z_{1cr} P_1\left(g_0(0) - g_2(0) + g_3(0) + s^2 z_{1cr}\right) + 16i s^2 z_{1cr} C_3$$
$$- 24\omega_0^3 z_{1cr} P_2 - 2\omega_0 z_{1cr}^3 s^2 - 8P_1\omega_0 r_0 + 16i P_1\omega_0^2 C_2\}/8$$
$$+ 2i\omega_0 P_2\left(g_2(0) - g_0(0) - g_3(0)\right) - 6i P_3\omega_0^3.$$

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