

A mathematical model of crystallization in an emulsion

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A mathematical model incorporating many of the important processes at work in the crystallization of emulsions is presented. The model describes nucleation within the discontinuous domain of an emulsion, precipitation in the continuous domain, transport of monomers between the two domains, and formation and subsequent growth of crystals in both domains. The model is formulated as an autonomous system of nonlinear, coupled ordinary differential equations. The description of nucleation and precipitation is based upon the Becker–Döring equations of classical nucleation theory. A particular feature of the model is that the number of particles of all species present is explicitly conserved; this differs from work that employs Arrhenius descriptions of nucleation rate. Since the model includes many physical effects, it is analyzed in stages so that the role of each process may be understood. When precipitation occurs in the continuous domain, the concentration of monomers falls below the equilibrium concentration at the surface of the drops of the discontinuous domain. This leads to a transport of monomers from the drops into the continuous domain that are then incorporated into crystals and nuclei. Since the formation of crystals is irreversible and their subsequent growth inevitable, crystals forming in the continuous domain effectively act as a sink for monomers “sucking” monomers from the drops. In this case, numerical calculations are presented which are consistent with experimental observations. In the case in which critical crystal formation does not occur, the stationary solution is found and a linear stability analysis is performed. Bifurcation diagrams describing the loci of stationary solutions, which may be multiple, are numerically calculated. © 2005 American Institute of Physics.

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I. INTRODUCTION

Nucleation and precipitation processes are notoriously hard to predict, describe, and control. They typically involve the transient existence of microscopic species that makes the process hard to observe and quantify. Once aggregates (clusters) of observable sizes have formed, they have typically been subject to growth processes dissimilar to the initial formation steps. In addition, in an experimental, industrial, or naturally occurring crystallization there may be several interacting processes at work.

This paper considers the nucleation and precipitation processes, and the subsequent formation and growth of crystals, within an emulsion. Specifically, we consider an emulsion consisting of liquid drops of an organic melt (e.g., oil) within an aqueous domain and the drops are stabilized with a surfactant. The organic melt is sparingly soluble in the aqueous domain. We consider the situation in which there is a tendency for the melt in the drops to nucleate and for the organic melt in the aqueous domain to precipitate. This situation can arise in an industrial crystallization process where one is attempting to manufacture separate small crystals of the organic compound.

Suppose that the nuclei of the organic melt precipitate and crystal formation and growth occur exclusively in the aqueous domain, the depletion of monomer concentration below the equilibrium concentration at the curved surface of the drops gives rise to a diffusional drive of monomers from the drops into the aqueous domain. The monomers entering the aqueous domain may attach themselves to the crystals there and the process continues, perhaps until the drops have completely evaporated. Now consider the converse situation in which crystals form and grow only in the drops. Monomers incorporated into crystals are fixed and may not move into the aqueous domain. However, if the concentration of monomers in the aqueous domain is not at the equilibrium concentration at the curved surface, monomers may enter or leave the drops, which affects crystal formation and growth. These two situations represent only the extremes of a continuum of possible behaviors.

The model we have developed is kinetic and no explicit appeal is made to chemical thermodynamics. The reason for this is that nucleation and crystal growth is an inherently transient phenomenon and such time dependence cannot be treated using equilibrium arguments. The model of the nucleation and precipitation processes is based upon the Becker–Döring equations of classical nucleation theory.¹ The Becker–Döring equations, however, are very complex (they

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consist, in principle, of an infinite sequence of ordinary differential equations) and their adoption would prevent the development of a tractable model. In the past, this has limited their application to unduly idealized situations. It is for this reason that a simplified, so-called contracted, model of the nucleation/precipitation process has been adopted. The use of this model is justified upon the basis of some important results² and is described in the next section.

Once critical nuclei are formed, they grow into crystals. There are several mechanisms involved in this process and the model developed here treats them crudely. The crystals are assumed simply to grow either at a constant rate or at a rate determined by the kinetics of the process, whereby the monomers are incorporated into the forming crystal. The rates of crystal growth are different in the drops and aqueous domain. The precise laws describing crystal growth probably do not qualitatively affect the results of the model; the important point is that they deplete the monomer concentration. The model of the transport of monomers between the drops and aqueous domain through the surfactant is, by necessity, *ad hoc* and may be sensitively dependent upon the surfactant-monomer interaction. We consider diffusion-limited transport of monomer, which is that used in the Lifshitz–Slyozov–Wagner theory of coarsening (Ostwald ripening),^{3,4} and chemical kinetic-limited transport of monomer.^{5–7}

In Sec. II, the mathematical model is developed and discussed. Since the model incorporates a number of physical processes, in Sec. III several special cases are considered, the reduced model equations solved, and the results discussed. Concluding remarks are made in Sec. IV.

II. MATHEMATICAL MODEL

The classical theory of nucleation rests upon the Becker–Döring (BD) equations describing the coagulation and fragmentation of clusters. They are a special case of the Smoluchowski equations (see, for example, van Dongen⁸) in that they allow growth (decay) of clusters only by the addition (removal) of individual particles or monomers (e.g., atoms, molecules, etc.)

The BD equations describe the dynamics of the following process:

$$C_r + C_1 \rightleftharpoons C_{r+1}, \quad (1)$$

where C_1 is a monomer, C_r is a cluster consisting of r monomers and C_{r+1} is a cluster consisting of $r+1$ monomers. Denoting the concentration of monomers with c_1 and the r th cluster ($r > 1$) by c_r , we write the BD equations describing the process as

$$\dot{c}_1 = -J_1 - \sum_{r=1}^{\infty} J_r, \quad (2)$$

$$\dot{c}_r = J_{r-1} - J_r, \quad (3)$$

$$J_r = a_r c_r c_1 - b_{r+1} c_{r+1}. \quad (4)$$

The final equation prescribes a form for J_r , the flux from clusters of size r to $r+1$. The rate at which a monomer at-

taches to an r cluster is proportional to the concentrations of each, the kinetic coefficient a_r being independent of time. The breakup of an $r+1$ cluster is spontaneous, and therefore the rate at which r clusters are formed by this process is proportional to the concentration c_{r+1} , the coefficient again being treated as time-independent. Various forms for the rate constants have been postulated, the most widely used are derived from the diffusion or the ballistic model. In the original studies of the BD equations,¹ the monomer concentration was held fixed, the so-called pool chemical approximation. This has the significant advantage that the equations are then linear. In contrast to this, we consider the case in which the total number of particles is held fixed [Eq. (2)] and retained, and the system thermodynamically closed.

A significant impediment to the analysis of the above system is that there are an infinite number of (ordinary) differential equations. Recent work² has led to a systematic, mathematically convincing, way of simplifying this system using a renormalization procedure. The essential idea is to develop a coarse-grained model of the process in which only the evolution of ranges of cluster sizes are considered. The required simplification of the system is obtained using a so-called maximal contraction of the equations. In this case, we track, for example, the concentration of monomers c_1 and representative concentrations of clusters in the range $C_2 - C_{\lambda_1 > 2}, \dots, C_{\lambda_i + 1} - C_{\lambda_{i+1} > \lambda_i + 1}, C_{\lambda_{i+1} + 1} - C_{\infty}$. The crucial feature is that the final range consists of a countably infinite number of cluster sizes, and thus the number of differential equations describing the nucleation kinetics becomes finite.

The nucleation equations we shall consider in this paper correspond to the simplest maximal contraction of the BD equations and are

$$\frac{dc_1}{dt} = -kp(c_1^p - \gamma c_p), \quad (5)$$

$$\frac{dc_p}{dt} = k(c_1^p - \gamma c_p). \quad (6)$$

These equations describe homogeneous nucleation and we track only the evolution of the monomer concentration c_1 and clusters containing p or fewer monomers c_p . We interpret p as the number of monomers in a nucleus which make it observable, for example, to strong x-ray scattering,⁹ and thus p may correspond to a precritical nuclei. Where precritical nuclei are not observable but crystals are observed, we set p equal to the number of monomers in a critical nucleus. In this case, we estimate p using equilibrium thermodynamics; several expressions for the critical radius of a nucleus exist for its formation from a melt or solution; (see, for example, Dunning¹⁰). The concentrations evolve from some initial values according to the above kinetic equations and nucleation corresponds to a sharp increase in c_p , i.e., an increase in the number of observable nuclei. Typically there is some time before c_p becomes observably large (which happens quite suddenly); this is called the nucleation induction time and can vary from the order of microseconds to days or even longer. That these equations have a unique, globally stable, stationary solution has been shown.²

Adoption of this model, and its generalizations outlined in this paper, implies conservation of the *total number* of monomers, which may be in the molten drop or the aqueous domain as monomers, clusters, or crystals. This is a departure from much work on nucleation/precipitation which uses Arrhenius rate laws for the nucleation rate J , such as $J = C \exp(-\Delta F/KT)$, where C is a constant, ΔF is the difference in Helmholtz free energy associated with the formation of a critical nucleus from the separate monomers, and k is Boltzmann's constant. In the classical theory of nucleation (see, for example, Dunning¹⁰) the Arrhenius nucleation rate is determined by finding the steady-state solution of the BD equations with *constant* monomer concentration and calculating the flux of monomers through the different cluster size classes using the Gibbs–Thompson equation for the partial pressure of a given cluster size. In the original formulation, the constant monomer concentration was maintained by decomposing clusters of a critical size into monomers. However, since critical nuclei grow into crystals rather than decompose into monomers, the assumptions underlying the calculation of the Arrhenius nucleation rate cannot be met without a constant influx of monomers into the system such as, for example, could be supplied in a well-stirred tank reactor. Although the assumption of constant monomer concentration may be appropriate in many situations, it is not applicable to the processes we model in this paper; the transport of monomers between the drops and aqueous domain and their incorporation into crystals are mutually dependent. A combinatorial model of nucleation and crystal growth using the Arrhenius relationship for nucleation rate in a disperse liquid (emulsion) is given by Kashchiev *et al.*¹¹ In the following sections, we generalize the contracted BD model of nucleation/precipitation to include crystal formation and growth, and transport of monomers between the drops and aqueous domain.

Once critical nuclei have formed, the formation of crystals is inevitable. The addition of a single monomer to a critical nucleus creates, by our definition, a crystal. The formation of a crystal involves an internal restructuring process. As a result of this restructuring, which we do not explicitly model, the subsequent growth of a crystal is quite different from the formation of the critical nucleus. Subsequent growth results in a monotonic decrease in Helmholtz free energy.¹⁰ Many processes are potentially important to this growth, for example, the incorporation of monomers into a growing face, dissipation of heat of fusion, and extraction of impurity. From the point of view of our model development, however, the crucial feature of crystal formation and growth from critical nuclei is that these processes are irreversible and the crystals constitute a separate solid phase. If p is the number of monomers in a cluster which make it a critical nucleus, then the rate of crystal formation \mathcal{F}_{cf} is given by

$$\mathcal{F}_{\text{cf}} = k_f(aV)(bV), \quad (7)$$

where V is the volume of melt or aqueous domain and k_f is a constant of proportionality; a and b are the monomer and critical nuclei concentrations, respectively. This law expresses that the number of crystals formed is proportional to the number of monomers and the number of critical nuclei

present. Setting N_{cry} equal to the number of crystals, we have

$$\frac{dN_{\text{cry}}}{dt} = \mathcal{F}_{\text{cf}} \quad (8)$$

Once these crystals form, they grow by the absorption of monomers, which occurs at some rate g . The rate at which monomers are absorbed into the crystals is \mathcal{F}_g , given by

$$\mathcal{F}_g = N_{\text{cry}}g. \quad (9)$$

The rate at which a crystal grows, g , is taken either to be constant or limited by the rate of incorporation of a monomer into a growing face (aggregation-limited). This latter rate is often parametrized into the form¹²

$$g = \begin{cases} K_G A (a - a^*)^m & (a > a^*) \\ 0 & (a \leq a^*) \end{cases}. \quad (10)$$

In this expression, K_G is a lumped parameter which includes the coefficient of mass transfer by diffusion (unlikely to be important in a melt) and a rate constant for the surface incorporation process; A is an $\mathcal{O}(1)$ constant inserted to account for geometry; m is a positive-order parameter which is experimentally determined; and a^* is the equilibrium saturation concentration in contact with the bulk-solid phase. For growth from a melt, a^* is the equilibrium concentration of monomers in the melt adjacent to the bulk solid.

Since the crystals comprise a separate phase, as they grow in volume it follows that the volume of the melt or aqueous domain must correspondingly shrink. Thus

$$\frac{dV}{dt} = -(p+1)v_m\mathcal{F}_{\text{cf}} - v_m\mathcal{F}_{\text{cg}}, \quad (11)$$

where v_m is the volume of a monomer, and we have assumed that there is no change in the volume of a crystal due to internal restructuring processes.

We now consider the transport of monomers between the aqueous domain and the drops without crystal formation and growth, a process we shall refer to as ripening but which should not be confused with Ostwald ripening or coarsening. We assume that all of the drops are of the same volume V_{drop} and are spherical. Since this excludes competitive diffusion, the number of drops N_d remains constant and coarsening does not occur.

We require an equation describing the transport of monomers between the drops and aqueous domain. We consider two functional forms for this, corresponding to diffusion-limited transport or (chemical) kinetic-limited transport. In the diffusion-limited transport, the rate-limiting step is the time for monomers to diffuse to or from the drop surface to the bulk solution. This is the situation considered by Lifshitz and Slyozov³ and Wagner⁴ (LSW) in the development of a theory of coarsening; we summarize some of their arguments below. A discussion of some issues related to this approach to the transport of monomers can be found in Mozyrsky and Privman.¹³ In particular, in the diffusion limit, the role of the surfactant is minimal. The alternative we consider is that in which the interaction of the surfactant with a

monomer is the rate-controlling process. This has been considered in a series of papers by Sugimoto⁵⁻⁷ on his kinetic-limited theory of coarsening.

Following the LSW theory of coarsening, we consider the diffusion-limited transport to be of the form

$$\mathcal{F}^{\text{LSW}} = N_d(R_{\text{attach}} - R_{\text{detach}}), \quad (12)$$

where R_{attach} is the rate of attachment of monomers to a drop and R_{detach} is the rate of detachment of monomers from a drop.

The steady-state probability-per-unit time that one of the diffusing monomers will strike a given drop is calculated by solving the diffusion equation for the monomer concentration with an absorbing boundary condition (zero monomer concentration) at the surface of the drop and with the monomer concentration at infinity equal to the overall monomer concentration α . The steady-state solution satisfying these conditions is $(1-R/r)\alpha$, where r is the distance from the center of the sphere of radius R . From this we calculate the rate at which monomers strike the drop to be

$$R_{\text{attach}} = 4\pi DR\alpha, \quad (13)$$

where D is the diffusivity of the monomers. The rate at which monomers leave the drop can be calculated by putting a sink of monomers at infinity and setting their concentration at the surface of the drop equal to the equilibrium value. The equilibrium concentration of monomers at the curved surface of the drop can be calculated from the (linearized) Gibbs-Thompson relation to be $\alpha_{\text{eqm}} = \alpha_{\infty}(1 + \Gamma/R)$, where α_{∞} is the equilibrium concentration adjacent to a plane surface and Γ is a constant (at constant temperature) proportional to the surface tension. The solution of the steady-state diffusion problem is $\alpha_{\infty}(1 + \Gamma/R)R/r$, and thus the rate of losing particles from the drop is

$$R_{\text{detach}} = 4\pi D\alpha_{\infty}(R + \Gamma), \quad (14)$$

where

$$\Gamma = \frac{2\sigma v_m}{k_B T}, \quad (15)$$

where σ is the surface tension, T is the temperature and k_B is the Boltzmann's constant. Since we have made no explicit assumption about the manner in which the monomers diffuse, micellar diffusion (the transport of monomers within micelles) is simply accommodated by modifying the value of D (provided that micellar diffusion satisfies Fick's law).¹⁴ Expressing the flux \mathcal{F}^{LSW} in terms of the volume of the drop, we have

$$\mathcal{F}^{\text{LSW}} = 4\pi D \left(\left(\frac{3V_{\text{drop}}}{4\pi} \right)^{1/3} (\alpha - \alpha_{\infty}) - \alpha_{\infty}\Gamma \right). \quad (16)$$

The assumption of chemical kinetic-limited transport implies that the above diffusion processes occur more rapidly than the attachment/detachment of monomers into/out of a drop. The factor determining if there is a net attachment or detachment of monomers into/out of a drop is the difference between the monomer concentration in the aqueous phase and the equilibrium monomer concentration at the curved

drop surface, $\alpha - \alpha_{\text{eqm}}$. However, the net rate of attachment/detachment is determined by the precise mechanisms of the attachment and detachment processes, which can be considered to be chemical reactions. If the transport of monomers is found to be chemically kinetic limited, the characterization of these attachment and detachment reactions may become important. Since we are not concerned here with a particular system, we shall assume that the attachment/detachment processes can be described using the same rate law. In particular, we assert that the net rate of attachment/detachment is given by the commonly-used reaction-limited transport equation,

$$\mathcal{F}^k = -N_d B \text{Sgn}[\alpha - \alpha_{\text{eqm}}] |\alpha - \alpha_{\text{eqm}}|^h, \quad (17)$$

e.g., Gray and Scott,¹⁵ where B and h are appropriate positive constants and Sgn is the function returning the sign of its argument (inserted to account for h even).

Finally, we incorporate all of the processes described above into one model that describes nucleation in the drops, precipitation in the aqueous domain, crystal formation and growth in both domains, and ripening. Writing the concentration of monomers as $a = N_1/V$ where N_1 is the number of monomers, we have $\delta a = \frac{\delta N_1}{V} - \frac{N_1}{V} \frac{\delta V}{V}$, where $\delta V = v_m \delta N_1 + p v_m \delta N_p$, and N_p is the number of nuclei. Using this and the analogous results for the monomers in the aqueous domain and nuclei in both domains, it is straightforward to develop the model equations. The full model is

$$\frac{da}{dt} = -k_0 p (a^p - \gamma_0 b) - \frac{(1 - a(p+1)v_m)}{V} \mathcal{F}_{\text{cf}}^d - \frac{(1 - av_m)}{V} \left(\mathcal{F}_{\text{cg}}^d - \frac{\mathcal{F}}{N_d} \right), \quad (18)$$

$$\frac{db}{dt} = k_0 (a^p - \gamma_0 b) - \frac{(1 - b(p+1)v_m)}{V} \mathcal{F}_{\text{cf}}^d + \frac{bv_m}{V} \left(\mathcal{F}_{\text{cg}}^d + \frac{\mathcal{F}}{N_d} \right), \quad (19)$$

$$\frac{dN_{\text{cry}}^d}{dt} = \mathcal{F}_{\text{cf}}^d, \quad (20)$$

$$\frac{dV}{dt} = -(p+1)v_m \mathcal{F}_{\text{cf}}^d - v_m \left(\mathcal{F}_{\text{cg}}^d + \frac{\mathcal{F}}{N_d} \right), \quad (21)$$

$$\frac{dV_{\text{drop}}}{dt} = -v_m \frac{\mathcal{F}}{N_d}, \quad (22)$$

$$\frac{d\alpha}{dt} = -k_1 q (\alpha^q - \gamma_1 \beta) - \frac{(1 - \alpha(q+1)v_m)}{(V_{\text{tot}} - N_d V_{\text{drop}})} \mathcal{F}_{\text{cf}}^{\text{aq}} - \frac{(1 - \alpha v_m)}{(V_{\text{tot}} - N_d V_{\text{drop}})} (\mathcal{F}_{\text{cg}}^{\text{aq}} + \mathcal{F}), \quad (23)$$

$$\frac{d\beta}{dt} = k_1(\alpha^q - \gamma_1\beta) - \frac{(1 - \beta(q+1)v_m)}{(V_{\text{tot}} - N_d V_{\text{drop}})} \mathcal{F}_{\text{cf}}^{\text{aq}} + \frac{\beta v_m}{(V_{\text{tot}} - N_d V_{\text{drop}})} (\mathcal{F}_{\text{cg}}^{\text{aq}} - \mathcal{F}), \quad (24)$$

$$\frac{dN_{\text{cry}}^{\text{aq}}}{dt} = \mathcal{F}_{\text{cf}}^{\text{aq}}, \quad (25)$$

$$\frac{dV_{\text{cry}}^{\text{aq}}}{dt} = -(q+1)v_m \mathcal{F}_{\text{cf}}^{\text{aq}} - v_m \mathcal{F}_{\text{cg}}^{\text{aq}} + v_m \mathcal{F}, \quad (26)$$

where a is the concentration of monomers within a drop; b is the concentration of nuclei containing p monomers in a drop; α is the concentration of monomers within the aqueous domain; β is the concentration of nuclei containing q monomers in the aqueous domain; k_i and γ_i are rate coefficients; V_{tot} is the total volume of molecules of water plus monomers, nuclei, and crystals within the whole emulsion; and superscripts d or aq identify the rates of crystal formation and crystal growth and the number and volume of crystals appropriate to the drops and aqueous domain, respectively. If critical nuclei are not formed in one or both of the domains, the appropriate rate(s) of crystal formation is (are) set to zero and p and/or q (as required) is set to a value beneath that corresponding to a critical nucleus.

Before we proceed with solving the various model equations, we develop some expressions of conservation of the numbers of particles present. Since we have assumed that the densities of nuclei and crystals are identical, these are most easily obtained by considering the conservation of volume; where there are density differences, the changes to the equations are straightforward though involved.

The volume of the melt within a drop is $V = V_{\text{aq}} v_m + V_{\text{bp}} v_m$, whence

$$a + pb = \frac{1}{v_m}, \quad (27)$$

which is constant. Similarly, the volume of the aqueous domain is $V_{\text{aq}} = V_w + V_{\text{aq}} \alpha v_m + V_{\text{aq}} q \beta v_m$, where V_w is the volume of all of the molecules of water present and is constant. Rearranging, we have

$$\alpha + q\beta = \frac{1}{v_m} \left(1 - \frac{V_w}{V_{\text{aq}}} \right). \quad (28)$$

Additionally, we can express the volume of the melt in a drop as

$$V = V_{\text{drop}} - V_{\text{cry}}^d \quad (29)$$

and the volume of the aqueous phase as

$$V_{\text{aq}} = V_{\text{tot}} - N_d V_{\text{drop}} - V_{\text{cry}}^{\text{aq}}. \quad (30)$$

The volumes of crystals present in both domains may be calculated from the integral expressions

$$V_{\text{cry}}^d(t) = v_m \int_0^t N_{\text{cry}}^d(t-s) g_d(s) ds + (1+p)v_m N_{\text{cry}}^d(t), \quad (31)$$

$$V_{\text{cry}}^{\text{aq}}(t) = v_m \int_0^t N_{\text{cry}}^{\text{aq}}(t-s) g_{\text{aq}}(s) ds + (1+q)v_m N_{\text{cry}}^{\text{aq}}(t). \quad (32)$$

Using these constraints, it is easily shown that the total number of monomers N is conserved, where

$$N = N_d V(a + pb) + N_d \frac{V_{\text{cry}}^d}{v_m} + V_{\text{aq}}(\alpha + q\beta) + \frac{V_{\text{cry}}^{\text{aq}}}{v_m}. \quad (33)$$

We obtain

$$\frac{dN}{dt} = N_d \dot{V}(a + pb) + N_d \dot{V}(\dot{a} + \dot{b}) + N_d (\dot{V}_{\text{drop}} - \dot{V})/v_m + \dot{V}_{\text{aq}}(\alpha + \beta) + V_{\text{aq}}(\dot{\alpha} + q\dot{\beta}) + \dot{V}_{\text{cry}}^{\text{aq}}/v_m \quad (34)$$

using Eq. (29)

$$\frac{dN}{dt} = N_d \dot{V}/v_m + N_d \dot{V}_{\text{drop}}/v_m - N_d \dot{V}/v_m + \dot{V}_{\text{aq}}(1 - V_w/V_{\text{aq}})/v_m + V_{\text{aq}}(V_w \dot{V}_{\text{aq}}/V_{\text{aq}}^2)/v_m + \dot{V}_{\text{cry}}^{\text{aq}}/v_m \quad (35)$$

using Eqs. (27) and (28), and

$$\frac{dN}{dt} = 0 \quad (36)$$

using Eq. (30)

III. NUMERICAL CALCULATIONS AND DISCUSSION

The model introduced in the preceding section describes several processes and includes many parameters. In the following sections, we consider successively more complete models in order to develop an understanding of the interaction of the processes included in the model.

A. Nucleation and crystal formation in one domain

Here we consider the model describing nucleation kinetics and crystal formation and growth in one domain only. Only in the absence of crystal formation does an exact, closed-form solution exist. In order to reduce the number of parameters and highlight dominant balances, we nondimensionalize the model equations. This has the added advantage that numerical calculations with extreme parameter values (which can lead to significant truncation and propagation errors) can be avoided. Although in this section we consider the processes involved in the melt that is in a drop, the case of precipitation of melt in the aqueous system is a trivial extension. We choose a concentration scale $1/v_m$, the concentration a of a drop containing only monomers, then $\bar{a} \in [0, 1]$ and $\bar{b} \in [0, 1/p]$, where the overbars indicate the dimensionless quantities. There are four time scales present

$$\tau_1 = \frac{1}{k_0 \gamma_0}, \quad \tau_3 = \frac{v_m^{p-1}}{k_0}, \quad \tau_5 = \frac{v_m^2}{V_{\text{aq}}^* k_f}, \quad \tau_7 = \frac{1}{g}, \quad (37)$$

which we interpret as follows: τ_1 is the time scale for a cluster in the drop to fragment; τ_3 is the time scale for a monomer in the drop to aggregate; τ_5 is the time scale for the formation of a crystal from a critical nucleus; and τ_7 is the

time scale for the growth of a crystal. In these expressions, g is a typical growth rate of the crystals and V^* is a characteristic volume scale for the drops. Nondimensionalizing, using τ_1 , V^* , and our new concentration scale, the reduced model equations become

$$\frac{da}{dt} = -p\Gamma_3^1 a^p + pb - \varepsilon\Gamma_5^1(1-a(p+1))abV - \varepsilon\Gamma_7^1 \frac{1-a}{V} N_{\text{cry}}^d g_d, \quad (38)$$

$$\frac{db}{dt} = \Gamma_3^1 a^p - b - \varepsilon\Gamma_5^1(1-b(p+1))abV + \varepsilon\Gamma_7^1 \frac{b}{V} N_{\text{cry}}^d g_d, \quad (39)$$

$$\frac{dN_{\text{cry}}^d}{dt} = \Gamma_5^1 abV^2, \quad (40)$$

$$\frac{dV}{dt} = -(p+1)\varepsilon\Gamma_5^1 abV^2 - \varepsilon\Gamma_7^1 N_{\text{cry}}^d g_d, \quad (41)$$

where we have dropped overbars for convenience,

$$\varepsilon = \frac{v_m}{V^*}, \quad (42)$$

and the dimensionless parameters Γ_i^1 are ratios of time scales

$$\Gamma_3^1 = \frac{\tau_1}{\tau_3}, \quad \Gamma_5^1 = \frac{\tau_1}{\tau_5}, \quad \Gamma_7^1 = \frac{\tau_1}{\tau_7}. \quad (43)$$

This model of nucleation, crystal formation, and crystal growth has no stationary solutions. The crystals form and grow until the whole of the drop is crystalline (with constant growth rate) or $a = a^*$ (with aggregation-limited growth). The model does, however, predict the size distribution of crystals as a function of time, which remains fixed once crystallization has ceased. (Over time, we expect the size distribution of crystals in the crystalline drop to coarsen, but this effect is not included in the model.) We define $N_{\text{size}}(x, t)$ as the number density of crystals containing x monomers at time t . It is then evident that

$$N_{\text{size}}(x, t) = N_{\text{cry}}^d(t - \Delta t), \quad (44)$$

where Δt is the solution of

$$\int_{t-\Delta t}^t g_d(s) ds = x. \quad (45)$$

For the case in which g_d is a constant (which certainly would not be appropriate for the final stages of the freezing of the drop), the crystal size distribution is

$$N_{\text{size}}(x, t) = N_{\text{cry}}^d(t - x/g). \quad (46)$$

For aggregation-limited kinetics, $N_{\text{size}}(x, t)$ is easily determined from Eq. (44) by solving Eq. (45) numerically.

The equations defining the model of nucleation, crystal formation, and crystal growth in one domain can easily be solved numerically. The parameters we used are displayed in Table I. Choosing appropriate values for these parameters is

TABLE I. Parameters used in the integration of the equations modeling nucleation, crystal formation, and crystal growth in one domain.

Parameter	Value	Parameter	Value
Γ_3^1	10^2	p	100
Γ_5^1	10^2	g_d	1
Γ_7^1	10^3	a^*	10^{-2}
m	1	ε	10^{-7}

difficult because they contain rate constants that cannot be estimated without suitable experimental data, which we have been unable to find. Here, and elsewhere in this paper, we have chosen parameter values that we believe to be physically plausible; certainly, the model simulations demonstrate physically reasonable behavior. In Fig. 1, we display the results of a numerical integration of the above model with aggregation-limited growth from initial values defined in Table II. Clearly, the concentration of monomers a and critical nuclei a quickly evolve from the initial state to reasonably steady values. This sudden behavior is not apparent in the plots of the volume of melt and number of crystals formed. Until the final stages of the crystallization of the drop ($V \rightarrow 0$), the rate of crystal formation is relatively constant.

B. Nucleation/precipitation in both domains with ripening

In this section, we consider the model which couples the two domains with ripening but does not include crystal formation. We identify the time scales present and perform a nondimensionalization. We continue to use our concentration scale $1/v_m$ so that $\bar{\alpha} \in [0, 1]$ and $\bar{\beta} \in [0, 1/q]$, where the overbars indicate the dimensionless quantities. There are three additional time scales present:

$$\tau_2 = \frac{1}{k_1 \gamma_1}, \quad \tau_4 = \frac{v_m^{q-1}}{k_1}, \quad (47)$$

and τ_0 , characteristic of the transport time of monomers between the drops and aqueous domain,

$$\tau_0 = 1/\mathcal{F}^*, \quad (48)$$

where

$$\mathcal{F}^* = 4\pi N_d D \alpha_\infty \Gamma \quad (49)$$

for diffusion-limited transport and

$$\mathcal{F}^* = \frac{N_d B}{v_m^h} \quad (50)$$

for kinetic-limited transport. The time scale τ_2 is characteristic of the time taken for a cluster in the aqueous domain to fragment and τ_4 is the time scale for monomers in the aqueous domain to aggregate. We define a volume scale for the drops from the steady-state solution of Eq. (22) with diffusion-limited transport and setting $\alpha \rightarrow 1/v_m$, giving a volume scale

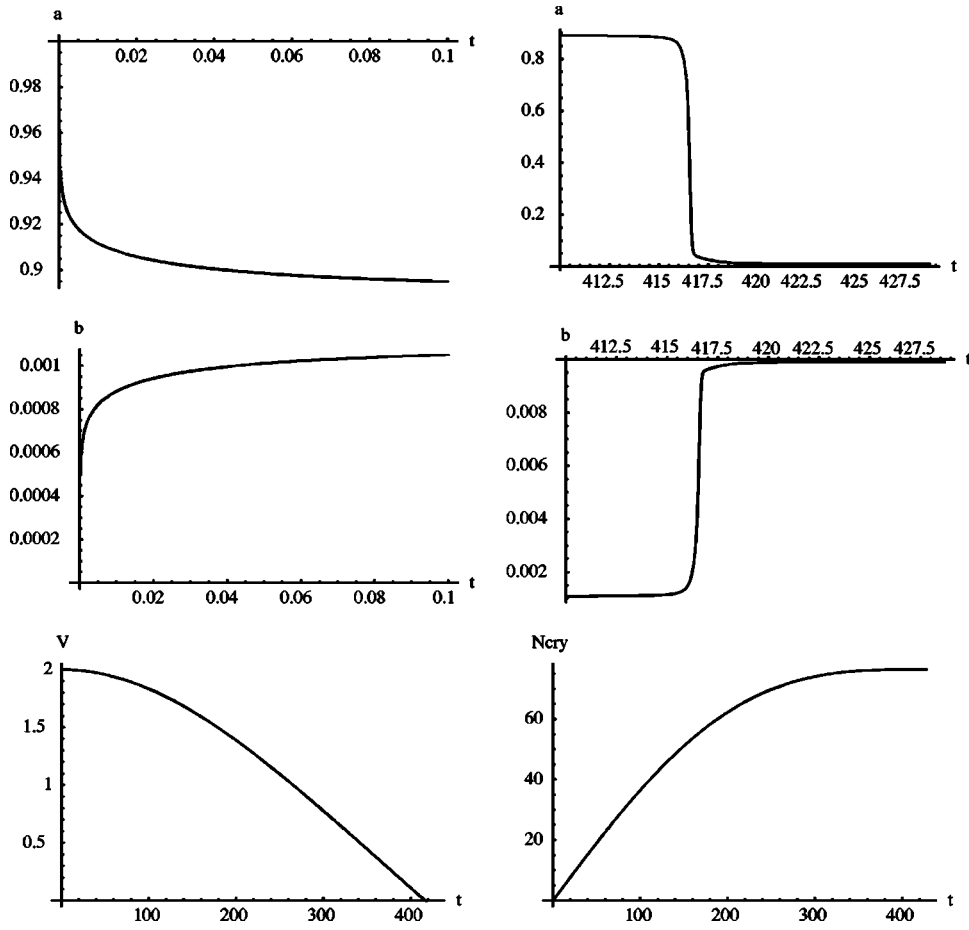


FIG. 1. Evolution of the concentrations of monomers a , critical nuclei b , volume of melt in one domain (the drops) only V , and number of crystals N_{cry} .

$$V^* = \frac{4}{3} \pi \left(\frac{\alpha_\infty \Gamma}{1/v_m - \alpha_\infty} \right)^3. \quad (51)$$

We scale V_{tot} , V_{aq} , and V_w with $N_d V^*$. Scaling time with τ_1 , we write the equations governing the nucleation/precipitation-ripening kinetics as

$$\frac{da}{dt} = -p(\Gamma_3^1 a^p - b) - \epsilon \frac{(1-a)}{V} \Gamma_0^1 \mathcal{F}, \quad (52)$$

$$\frac{db}{dt} = (\Gamma_3^1 a^p - b) + \epsilon \frac{b}{V} \Gamma_0^1 \mathcal{F}, \quad (53)$$

$$\frac{d\alpha}{dt} = -q(\Gamma_4^1 \alpha^q - \Gamma_2^1 \beta) + \epsilon \frac{(1-\alpha)}{V_{\text{tot}} - V} \Gamma_0^1 \mathcal{F}, \quad (54)$$

$$\frac{d\beta}{dt} = (\Gamma_4^1 \alpha^q - \Gamma_2^1 \beta) - \epsilon \frac{\beta}{V_{\text{tot}} - V} \Gamma_0^1 \mathcal{F}, \quad (55)$$

TABLE II. Initial values used for the integration of the equations modeling nucleation, crystal formation, and crystal growth in one domain.

Variable	Initial value	Variable	Initial value
a	1	V	2
b	0	N_{cry}	0

$$\frac{dV}{dt} = -\epsilon \Gamma_0^1 \mathcal{F}. \quad (56)$$

The new dimensionless parameters Γ_i^1 are

$$\Gamma_2^1 = \frac{\tau_1}{\tau_2}, \quad \Gamma_4^1 = \frac{\tau_1}{\tau_4}. \quad (57)$$

With these scalings, the constraints on the numbers of monomers present are

$$a + pb = 1 \quad (58)$$

within the drops and

$$\alpha + q\beta = 1 - \frac{V_w}{V_{\text{aq}}} \quad (59)$$

within the aqueous domain. Note that the last constraint implies that $\alpha < 1$. The dimensionless diffusion-limited flux is

$$\mathcal{F}^{\text{LSW}} = 1 + \left(\frac{\alpha_\infty - \alpha}{1 - \alpha_\infty} \right) V^{1/3}, \quad (60)$$

and the dimensionless chemical kinetic-limited flux is

$$\mathcal{F}^k = -\text{Sgn} \left[\alpha - \alpha_\infty + \frac{\alpha_\infty - 1}{V^{1/3}} \right] \left| \alpha - \alpha_\infty + \frac{\alpha_\infty - 1}{V^{1/3}} \right|^h. \quad (61)$$

Let us examine the fixed points, or stationary solutions, of the nucleation-ripening equations. It is immediately clear that

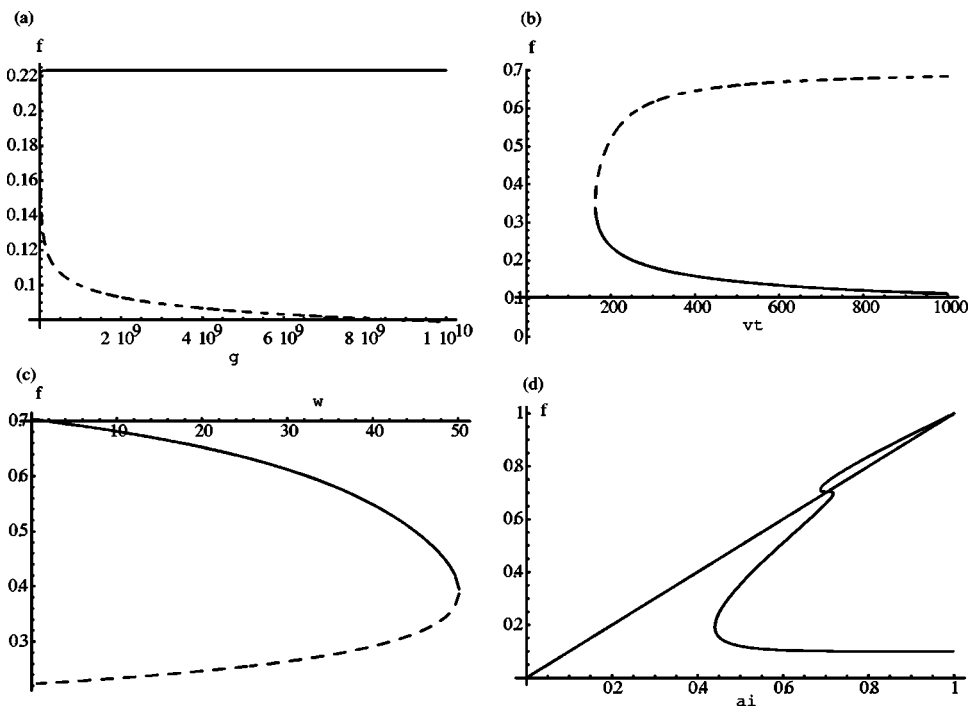


FIG. 2. Bifurcation diagrams showing the loci of stationary solutions α_{ss} versus (a) Γ_4^2 , (b) V_{tot} , (c) V_w , and (d) α_∞ . For diffusive and linear chemical kinetic-limited ripening, the solid line indicates asymptotic stability and the dashed line indicates asymptotic instability; for nonlinear kinetic-limited ripening, all of the solutions are stable.

$$b_{ss} = \Gamma_3^1 a_{ss}^p \quad \beta_{ss} = \Gamma_4^2 \alpha_{ss}^q, \quad (62)$$

where $\Gamma_4^2 = \tau_2 / \tau_4$, and

$$V_{ss} = \left(\frac{1 - \alpha_\infty}{\alpha_{ss} - \alpha_\infty} \right)^3 \quad (63)$$

(where the subscript *ss* stands for stationary solution). The expression for $V_{ss} = 4/3 \pi R_{ss}^3$ corresponds to the critical radius which occurs in the LSW theory of coarsening or Ostwald ripening. In this theory, drops with radius $R > R_{ss}$ grow and drops with radius $R < R_{ss}$ shrink. Since all the drops are of the same radius in the model we are considering, however, there is no competitive diffusion. Applying the constraints within the drop and aqueous domain yields the following equations for a_{ss} and α_{ss} :

$$a_{ss} = 1 - p \Gamma_3^1 a_{ss}^p \quad (64)$$

and

$$\Gamma_4^1 \alpha_{ss}^q = \frac{\Gamma_2^1}{q} \left(1 - \alpha_{ss} - \frac{V_w}{V_{tot} - V_{ss}} \right). \quad (65)$$

Substituting for V_{ss} in this latter equation and rearranging, we obtain

$$\alpha_{ss}^q \Gamma_4^2 ((\alpha_{ss} - \alpha_\infty)^3 V_{tot} - (1 - \alpha_\infty)^3) + \frac{1}{q} (V_w (\alpha_{ss} - \alpha_\infty)^3 - (1 - \alpha_{ss})(1 - \alpha_\infty)^3 + (1 - \alpha_{ss}) V_{tot} (\alpha_{ss} - \alpha_\infty)^3) = 0. \quad (66)$$

That Eq. (64) has a unique, real, positive solution can be seen as follows: the right-hand side of the equation is $f = 1 - p \Gamma_3^1 a_{ss}^p$: since $\Gamma_3^1 > 0$, $p > 1$, it follows that $df/da_{ss} < 0$ and thus intercepts the straight line a_{ss} at only one real value in $[0, 1]$.

The fixed-point solutions of Eq. (66), a $(q+3)$ th order polynomial, are not so easy to identify. Several analytical techniques exist which can be used to determine the number of fixed points $\alpha_{ss} \in [0, 1]$ (see, for example, Wilf¹⁶). However, the dependence of the polynomial's coefficients upon the several parameters makes application of these techniques impractical. Thus, we confine ourselves to a numerical investigation. Note that the stationary solutions do not depend upon the form of the flux law.

Since there is always a unique stationary solution a_{ss} and the value of V_{ss} is prescribed by α_{ss} [see Eq. (63)], we focus our attention upon the loci of stationary solutions α_{ss} as we vary the model parameters in Eq. (66) (bifurcation diagrams). We construct bifurcation diagrams of α_{ss} versus Γ_4^2 , V_{tot} , V_w , and α_∞ . A coarse grid was used with a conjugate gradient optimization method to determine the approximate location of turning points and hysteresis loops. Once these were found, a Newton-Raphson method was used to track the branches of stationary solutions as a function of the bifurcation parameter. The parameter space searched in this way was $0 < \alpha_\infty < 1$, $0 < V_w < 100$, $0 < V_{tot} < 10^3$, and $0 < \Gamma_4^2 < 10^{10}$ and $q = 10$.

Figure 2 shows the bifurcation diagrams obtained; except for the bifurcation parameter, the parameters used are given in Table III. These diagrams depict several interesting

TABLE III. Parameters used to determine the bifurcation diagrams. The upper set was used to determine the multiple solutions for α_{ss} ; the lower set uniquely defines a_{ss} .

Parameter	Value	Parameter	Value
α_∞	10^{-3}	V_{tot}	100
Γ_4^2	1	V_w	90
q	10		
Γ_3^1	10^2	p	10

features. There exist regions in the parameter space in which no stationary solutions exist at all. Numerical calculations indicate that these regions correspond to complete evaporation of the drops. As each bifurcation parameter is independently varied, branches of stationary solutions appear suddenly at so-called cusp catastrophes. The stability of these solution branches was determined numerically using a standard, linear perturbation technique. For diffusion-limited and linear kinetic-limited ripening, the asymptotically stable branches are depicted with a solid line and the asymptotically unstable with a dashed line; with nonlinear kinetic-limited ripening, both branches (solid and dashed) are stable.

In Fig. 2(a), Γ_4^2 , the rate of aggregation relative to fragmentation of clusters in the aqueous domain, is varied. This bifurcation diagram, though it depicts valid solutions of Eq. (66), does not, however, depict physically realizable stationary solutions. This is because these solutions correspond to a drop volume greater than the total volume of the aqueous and drop domains.

In Fig. 2(b), we see physically realizable stationary solutions of α_{ss} versus the total volume of the aqueous and drop domains. Perhaps surprisingly, increasing the total volume while keeping the volume of water constant (leading to, for example, a water-in-oil emulsion), leads to a stable stationary solution in which the monomer concentration in the aqueous domain decreases.

In Fig. 2(c), we see that decreasing the volume of water while keeping the total volume constant leads to a stable solution in which the monomer concentration in the aqueous domain increases. While this could perhaps be expected from the previous diagram, we stress that increasing the volume of oil is not reciprocal with an equivalent decrease in the volume of water. This is because the absolute volumes of oil and water must be compared with the volume of the drops. The final bifurcation diagram shows the variation of the stationary solution α_{ss} versus α_∞ . Only the part of the curve above $\alpha_{ss} = \alpha_\infty$ is physically realizable. The physical portion of the connecting path between the second and third turning points (reading left to right) is unstable. Suitable variation of parameters can bring the hysteresis loop entirely into the physical portion of the diagram. This could give rise to ignition or extinction in the rate of precipitation of the subcritical nuclei in the aqueous domain.

C. Crystal formation in both domains with ripening

The interaction between ripening, crystal formation, and crystal growth in both domains is explored in this section. The equations of the full model are expressed in nondimensional form as

$$\begin{aligned} \frac{da}{dt} = & -p\Gamma_3^1 a^p + pb - \varepsilon\Gamma_5^1(1-a(p+1))abV \\ & - \varepsilon\Gamma_7^1 \frac{1-a}{V} N_{\text{cry}}^d g_d - \varepsilon \frac{1-a}{V} \Gamma_0^1 \mathcal{F}, \end{aligned} \quad (67)$$

TABLE IV. Parameters used in the integration of the equations modeling nucleation, growth, and ripening.

Parameter	Value	Parameter	Value
Γ_6^1	10^2	α^*	10^{-2}
Γ_8^1	10^3	m_1	1
q	100	g_1	1
Γ_2^1	0.1		

$$\begin{aligned} \frac{db}{dt} = & \Gamma_3^1 a^p - b - \varepsilon\Gamma_5^1(1-b(p+1))abV \\ & + \varepsilon\Gamma_7^1 \frac{b}{V} N_{\text{cry}}^d g_d + \varepsilon \frac{b}{V} \Gamma_0^1 \mathcal{F}, \end{aligned} \quad (68)$$

$$\frac{dN_{\text{cry}}^d}{dt} = \Gamma_5^1 abV^2, \quad (69)$$

$$\frac{dV}{dt} = -(p+1)\varepsilon\Gamma_5^1 abV^2 - \varepsilon\Gamma_7^1 N_{\text{cry}}^d g_d - \varepsilon\Gamma_0^1 \mathcal{F}, \quad (70)$$

$$\frac{dV_{\text{drop}}}{dt} = -\varepsilon\Gamma_0^1 \mathcal{F}, \quad (71)$$

$$\begin{aligned} \frac{d\alpha}{dt} = & -q\Gamma_4^1 \alpha^q + q\Gamma_2^1 \beta - \varepsilon\Gamma_6^1(1-\alpha(q+1))\alpha\beta V_{\text{aq}} \\ & - \varepsilon\Gamma_8^1 \frac{1-\alpha}{V_{\text{aq}}} N_{\text{cry}}^{\text{aq}} g_{\text{aq}} + \varepsilon \frac{1-\alpha}{V_{\text{aq}}} \Gamma_0^1 \mathcal{F} \end{aligned} \quad (72)$$

$$\begin{aligned} \frac{d\beta}{dt} = & \Gamma_4^1 \alpha^q - \Gamma_2^1 \beta - \varepsilon\Gamma_6^1(1-\beta(q+1))\alpha\beta V_{\text{aq}} \\ & + \varepsilon\Gamma_8^1 \frac{\beta}{V_{\text{aq}}} N_{\text{cry}}^{\text{aq}} g_{\text{aq}} - \varepsilon \frac{\beta}{V_{\text{aq}}} \Gamma_0^1 \mathcal{F}, \end{aligned} \quad (73)$$

$$\frac{dN_{\text{cry}}^{\text{aq}}}{dt} = \Gamma_6^1 \alpha\beta V_{\text{aq}}^2 \quad (74)$$

$$\frac{dV_{\text{aq}}}{dt} = -(q+1)\varepsilon\Gamma_6^1 \alpha\beta V_{\text{aq}}^2 - \varepsilon\Gamma_8^1 N_{\text{cry}}^{\text{aq}} g_{\text{aq}} + \varepsilon\Gamma_0^1 \mathcal{F}, \quad (75)$$

where

$$\Gamma_6^1 = \frac{\tau_1}{\tau_6}, \quad \Gamma_8^1 = \frac{\tau_1}{\tau_8} \quad (76)$$

are the aqueous domain equivalents of Γ_5^1 and Γ_7^1 in the drop;

$$\tau_6 = \frac{v_m^2}{V^{*2} k_f^{\text{aq}}}, \quad \tau_8 = \frac{1}{g_1}, \quad (77)$$

where k_f^{aq} is the kinetic coefficient of crystal formation and g_1 is a characteristic crystal growth rate in the aqueous domain. The constants α^* and m_1 are the crystal growth parameters which play the equivalent role of a^* and m in Eq. (10). Note that in the expressions for \mathcal{F} , given in the previous section, we must set $V \rightarrow V_{\text{drop}}$.

TABLE V. Initial values used for the integration of the equations modeling nucleation, ripening, crystal formation, and crystal growth in both domains.

Variable	Initial value	Variable	Initial value
α	10^{-3}	V_{drop}	2
β	6.15×10^{-4}	$N_{\text{cry}}^{\text{aq}}$	0
V_{aq}	96		

We solve the equations with and without ripening in order to discern the effect of the transport of monomers between the drops and aqueous domain. The parameter values taken are those used in Secs. III A and III C, with the additional values and initial data given in Tables IV and V. In Fig. 3, we show the monomer and critical nuclei concentration in the drop, volume of melt, drop volume, and number of crystals formed in the drop. In Fig. 4, we show the monomer and critical nuclei concentration in the aqueous domain, the volume of the aqueous domain, and the number and volume of crystals in the aqueous domain. The solutions shown with a solid line include ripening; the dashed lines show the

solutions in which $\Gamma_0^1 \rightarrow 0$ and nucleation, crystal formation, and crystal growth occur in each domain separately.

With ripening, the monomer and critical nuclei concentration in the drops suddenly change as the drop volume approaches zero. This is because the removal of the last few monomers from the drop sharply decreases their concentration and consequently increases the concentration of critical nuclei. The loss of monomers from the drops due to ripening is reflected in the decrease in the number of crystals formed in the drops. Where there is no ripening, these effects do not occur and events in the drops follow the solutions presented in Sec. III A. The decrease in drop volume due to monomers being transported into the aqueous domain leads, in the aqueous domain, to an enhanced increase in monomer concentration from the initial value and to a consequent decrease in critical nuclei concentration. Ripening leads to an increase in the volume of the aqueous domain and enhances the number and volume of crystals in the aqueous domain.

From a state in which there are no nuclei in the drop or aqueous domain, perhaps after some transient time, there is

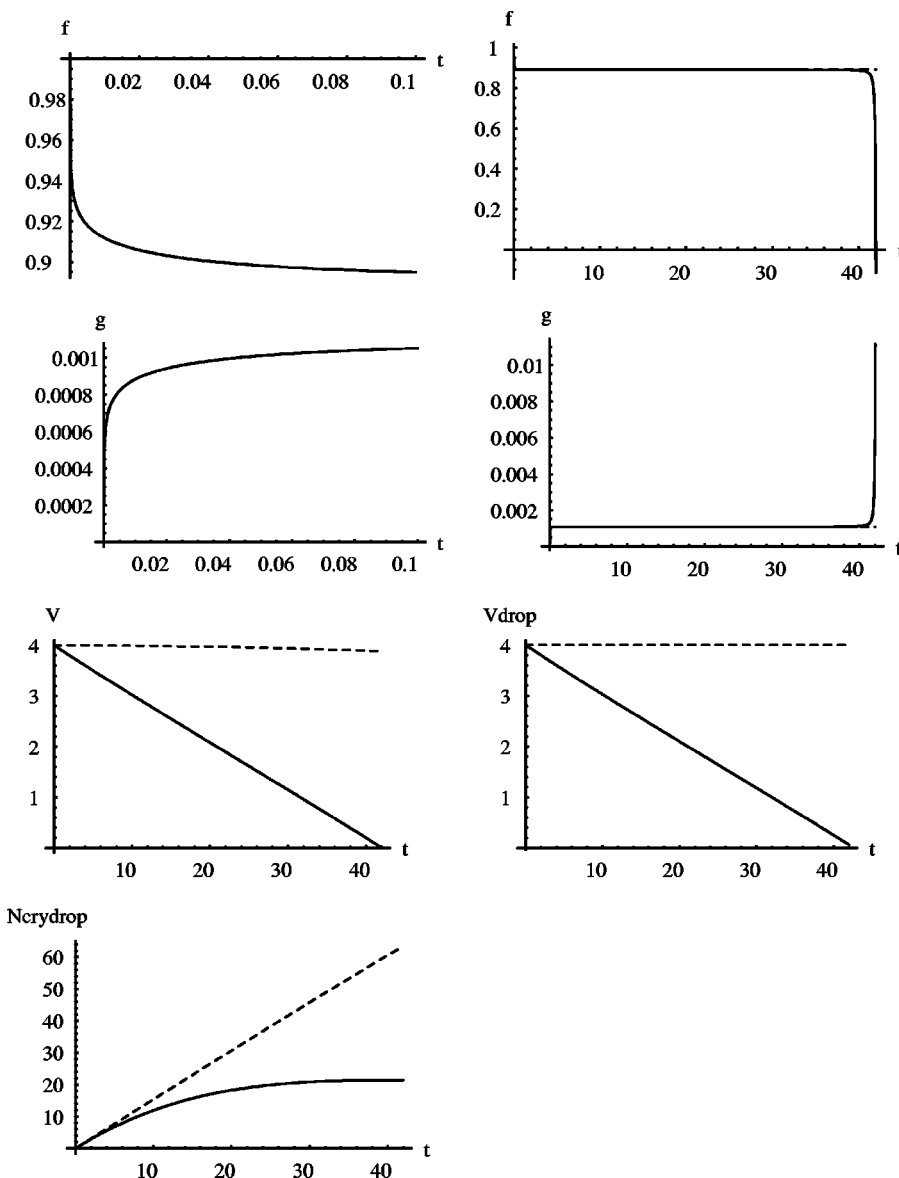


FIG. 3. Evolution of the concentrations of monomers and critical nuclei, volume of melt, drop volume, and number of crystals in the drop. The solutions depicted with a solid line include ripening; those with a dashed line do not.

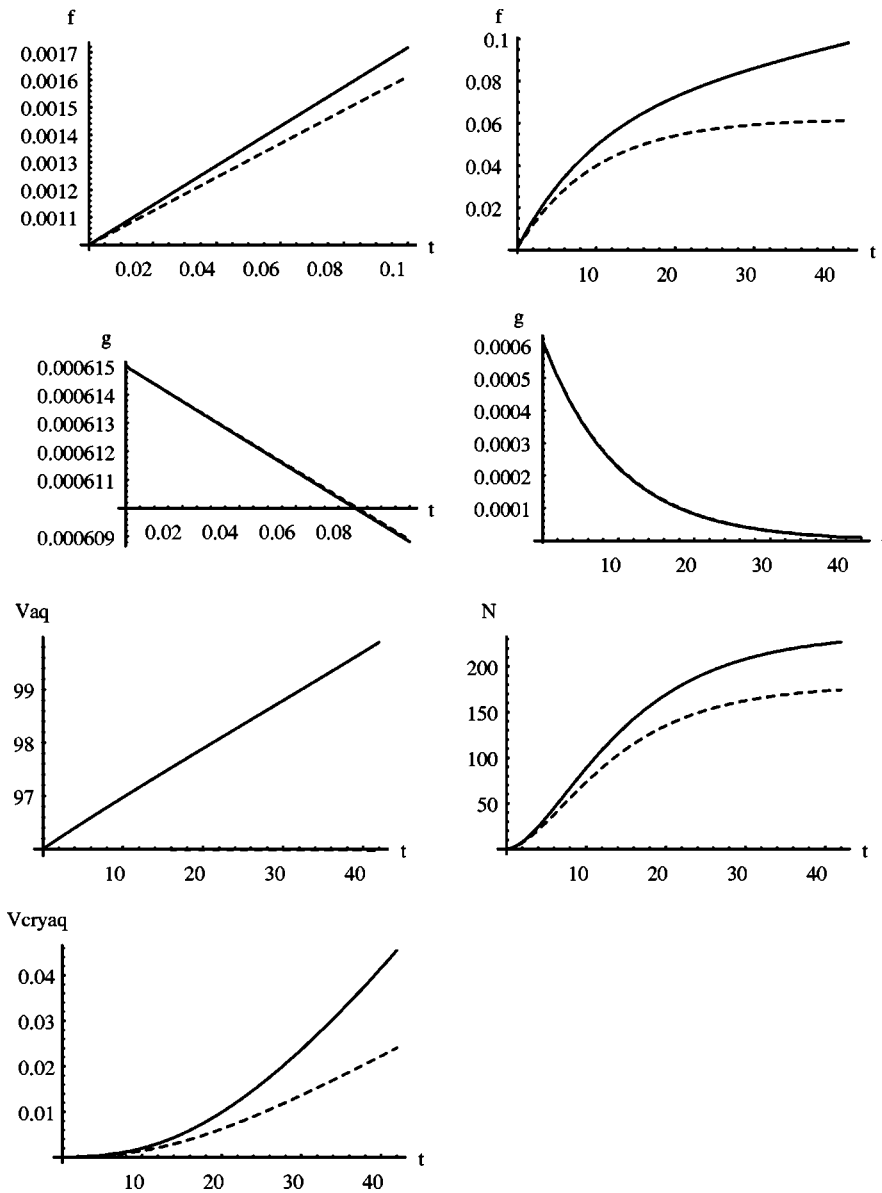


FIG. 4. Evolution of the concentrations of monomer and critical nuclei, volume of the aqueous domain, and number and volume of crystals in the aqueous domain. The solutions depicted with a solid line include ripening; those with a dashed line do not.

typically a net transport of monomers from the drop into the aqueous domain. This is because as nuclei form and crystals form and grow in the aqueous domain, the monomer concentration at the drop surface falls below the equilibrium concentration there. This leads to ripening and monomers are transported into the aqueous domain in order to bring the surface concentration closer to equilibrium. However, if the initial concentration of monomers in the drops is above the equilibrium concentration at the drop surface, there may be an initial transport of monomers *into* the drops. The dimensionless initial equilibrium concentration at the drop surface is

$$\alpha_{\text{crit}} = \alpha_{\infty} + \frac{1 - \alpha_{\infty}}{V_{\text{in}}^{1/3}}, \quad (78)$$

where V_{in} is the initial melt/drop volume. In order for monomers to initially leave the aqueous domain and enter the drops, a necessary condition is that the initial monomer concentration α_{in} must satisfy

$$\alpha_{\text{crit}} < \alpha_{\text{in}} \leq 1 - \frac{V_w}{V_{\text{tot}} - V} \equiv \alpha_{\text{max}}, \quad (79)$$

where α_{max} is the maximum obtainable monomer concentration in the aqueous domain. Provided that reaction rates are finite, this condition is also sufficient.

IV. DISCUSSION AND CONCLUDING REMARKS

A model has been developed which describes the formation of critical nuclei and crystals and their subsequent growth in a single domain, which may be a melt or a solution. This model predicts, as a function of time, the monomer and critical nuclei concentrations, and the number and total volume of crystals formed; from this the size distribution of crystals can be inferred. This model differs from a previous work in that the number of particles is explicitly conserved and the dynamical interactions of the processes are described with a closed set of coupled, nonlinear ordinary differential equations. The nucleation part of the model is based upon a contracted form of the BD equations: crystal formation is

based upon a ballistic model: and the growth of the crystals is based upon a well-known diffusion-aggregation limited parametrization.

This model was extended to consider the more complicated processes at work within an emulsion. Here, we have nucleation in the drops of melt, precipitation in the aqueous domain, and a transport of monomers (which may be extremely weak) between the two domains. We have considered diffusion-limited (LSW) and kinetic-limited transport of monomers. To the authors' knowledge, this is the first combined mathematical model of nucleation/precipitation and ripening in an emulsion. As revealed in the calculations of Sec. III C, the formation of nuclei and crystals in the aqueous domain lowers the monomer concentration there to below the equilibrium concentration at the surface of the drops. This leads to a transport of monomers from the drops into the aqueous domain which are then incorporated into crystals and nuclei. Since the formation of crystals is irreversible and their subsequent growth inevitable, crystals formed in the aqueous domain effectively act as a sink for monomers, sucking monomers from the drops. This phenomena helps to explain the observations¹⁷ in which metachloronitrobenzene migrated from the drops of an emulsion to form crystals in the aqueous domain, while the melt remaining in the drops became increasingly rich in parachloronitrobenzene.

The case in which critical nuclei do not form was also analyzed. Since there is no crystal formation (which is considered to be an irreversible process), there are stationary solutions to the model equations. These were numerically calculated and their stability determined. The multiplicity of stationary solutions echoes work on mixed suspension, mixed product removal (MSMPR) crystallization reactors.¹⁸ In fact, an analogy can be drawn between the emulsion and the MSMPR reactor system: the aqueous domain can be identified with the reactor; the flux of monomers from the drops represents the feed; and the formation of crystals is analogous to the product stream.

While the models presented in this paper are fairly complex, they represent a considerable simplification of the physical processes at work. In particular, by developing the model in terms of ordinary differential equations, we have implicitly assumed that the interior of the drops and aqueous domain are well mixed. Further, the spatial independence of the model means that no account of the geometry of the domains is taken. We have assumed that the two domains form an emulsion, with one domain dispersed, but the only point at which this is used is through the parametrized flux of monomers between the two domains. We have also parametrized the crystal growth process. The assumption that the number of drops remain constant and that all of the drops are of the same size removes the potential for competitive diffusion and hence for Ostwald ripening. Incorporation of this latter effect would considerably complicate the analysis. A more tractable extension would be to include the temperature dependence of the rate constants; this would require an additional equation expressing conservation of heat. In other simpler systems, such temperature dependence has led to multiple stationary states and complex time-dependent behavior.¹⁵

The model we have developed includes many of the important physical processes involved in crystallization in an emulsion. Although there are a number of parameters required for quantitative prediction, the parametric dependence of the model is straightforward to determine and the model describes the range of qualitative behavior possible.

ACKNOWLEDGMENT

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APPENDIX A: NOTATION

A	Geometrical factor of $\mathcal{O}(1)$
a, α	Monomer concentration within a drop (aqueous domain)
a_r	Kinetic coefficient in Becker–Döring equations
a_{ss}, α_{ss}	Nondimensional, stationary solution monomer concentration in a drop (aqueous domain)
$\alpha_{\text{eqm}}, \alpha_{\infty}$	Equilibrium monomer concentration adjacent to a curved surface (plane surface)
α_{crit}	Initial equilibrium concentration of monomers at drop surface in aqueous domain
α_{max}	Maximum obtainable monomer concentration in aqueous domain
a^*, α^*	Equilibrium saturation concentration in contact with bulk phase in a drop (aqueous domain)
B	Constants in expression of chemical-kinetic limited monomer transport
b, β	Concentration of nuclei containing p monomers in a drop (aqueous domain)
b_r	Kinetic coefficient in Becker–Döring equations
b_{ss}, β_{ss}	Nondimensional, stationary solution nuclei concentration in a drop (aqueous domain)
c_1	Concentration of monomer
c_p	Concentration of a cluster containing p monomers
γ_i	Rate coefficients in contracted Becker–Döring equations ($i=0, 1$)
$\Gamma_j^i = \tau_i / \tau_j$	Nondimensional parameter, a ratio of time scales
$\Gamma = 2\sigma v_m / (kT)$	Constant used for attachment/detachment calculations
D	Diffusivity of monomers of organic melt in the aqueous phase
$\epsilon = v_m / V^*$	Typical ratio of monomer to a drop (a small parameter)
F_{cf}	Rate of crystal formation
F_g	Rate at which monomers are absorbed into crystals
F^k	Chemical-kinetic limited transport of monomers into/out of drops
F^{LSW}	Diffusion-limited transport of monomers into/out of a drop according to the theory of Lifshitz and Slyozov and Wagner

- g, g_d, g_{aq} Rate at which crystal grows, in a drop, in aqueous domain
 h Constants in expression of chemical-kinetic limited monomer transport
 J_r Flux of clusters from size r to $r+1$
 k Kinetic coefficient in Becker–Döring equations
 k_i Rate coefficients in contracted Becker–Döring equations ($i=0, 1$)
 k_B Boltzmann's constant
 k_f, k_f^{aq} Rate coefficients for crystal formation in drop (aqueous domain)
 K_G Lumped parameter in aggregation-limited crystal growth rate
 m, m_1 Crystal growth parameter in a drop (aqueous domain)
 N_1, N_p Number of monomers (nuclei containing p monomers)
 N Total number of monomers in drops, aqueous domain and crystals
 N_{cry} Number of crystals
 N_d Number of drops (a constant)
 $N_{size}(x, t)$ Number of density of crystals in a drop containing x monomers at time t
 r Distance from center of a drop
 R Drop radius
 R_{attach} Rate at which monomers strike a drop
 R_{detach} Rate at which monomers leave a drop
 R_{ss} Stationary solution for a drop radius
 σ Surface tension of drop-aqueous domain surface
 t Time
 T Temperature (held constant in this paper)
 τ_1 Time scale for a cluster in a drop to fragment
 τ_3 Time scale for a monomer in a drop to aggregate
 τ_5 Time scale for formation of crystal from a critical nucleus in a drop
 τ_7 Time scale for growth of a crystal in a drop
 τ_0 Time scale for transport of monomer between drops and aqueous domain
 τ_2 Time scale for cluster in aqueous domain to fragment
 τ_4 Time scale for monomers in aqueous domain to fragment
 τ_6 Time scale for formation of crystal from a critical nucleus in aqueous domain
 τ_8 Time scale for growth of a crystal in aqueous domain
 V_{aq} Volume of aqueous domain
 V_{cry}^d, V_{cry}^{aq} Volume of crystals in a drop (aqueous domain)
 V_{drop} Volume of a drop of organic melt
 v_m Volume of monomer of organic melt
 V_{ss} Stationary solution for a drop volume
 V_{tot} Total volume of molecules of water plus monomers, nuclei, and crystals (assumed constant)
 V_w Volume of all molecules of water (constant)
 V^* Characteristic volume scale for a drop.

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