The Applicability of Catastrophe Theory to Emulsion Phase Inversion

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Catastrophe theory, in particular the elementary cusp catastrophe, has been successfully applied to describe the qualitative features of catastrophic phase inversion in emulsions, but quantitative, experimental tests of the cusp catastrophe did not yield satisfactory results. We have shown that the elementary butterfly catastrophe can fit experimental data from the literature with reasonable accuracy. The quality of the fit may be improved, but only at the cost of the introduction of more fit parameters with little or no physical significance. We present an expression derived from physical properties rather than mathematical ones, on the basis of which all observed catastrophic phenomena can be qualitatively described. At values of the interfacial tension typical to coarse emulsions, this model predicts phase separation. However, phase inversion is generally observed under these conditions. We point out that the assumptions that justify a thermodynamical treatment of transitional inversion are not valid for catastrophic inversion. Our conclusions indicate that catastrophic phase inversion, unlike transitional inversion, should be treated on a kinetic basis rather than a thermodynamical one. © 1995 Academic Press, Inc.

Key Words: emulsion; phase inversion; catastrophe theory; cusp catastrophe; butterfly catastrophe; interfacial Gibbs free energy.

INTRODUCTION

Phase inversion in emulsions is generally divided into two mechanisms: *transitional* and *catastrophic* inversion (1). Transitional inversion is induced by changing factors that affect the distribution of the emulsifier over the phases, such as, for instance, temperature, HLB of the emulsifier, salinity of the aqueous phase, and polarity of the organic phase. Catastrophic inversion is induced by increasing the fraction² of the dispersed phase and has the characteristics of a *catastrophe*. A catastrophe here means a sudden change in behavior of a system, as a result of gradually changing conditions. In practice, the term catastrophe might also refer to the mathematical description of catastrophic behavior.

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² Since the relationship between the characteristics of the normal factor A and the fraction of one of the phases of the emulsion is based exclusively on qualitative similarities, this fraction may be defined on a molar, mass, or volume basis. Unless explicitly stated otherwise, the term "fraction" in this paper will be applicable to molar and mass, as well as to volume fractions. In the field of emulsions, volume fractions are usually preferred.

Catastrophe theory, developed by Thom (2), is a mathematical framework to describe catastrophes. It distinguishes one or more *behavior parameters* (behavior space) and one or more *control parameters* (control space). The system obeys an optimization function, which is a function in the behavior space, parametrized by the control space. It is assumed that the system always exists under a locally optimum condition. The condition that all derivatives of the optimization function to the behavior space are zero describes a set in the total space (behavior space $\times$ control space), which represents all possible states of the system. For a given set of conditions (one point in the control space), there are one, several, or no possible behavior states (points in behavior space).

Catastrophes can occur at those points in control space where the number of possible behavior states differs from the number of possible behavior states at neighboring points, the so-called *singularities*. Here is also at least one second derivative of the optimization function to the behavior space equal to zero. The projection of the singularity set on the control space is called the *bifurcation*.

Catastrophe theory has been applied in various fields, for example, the behavior of a stock market, the stability of ships, or territorial behavior of fish. Zeeman (3) gives an overview of various applications and also provides an excellent introduction to catastrophe theory, avoiding mathematical formalisms as much as possible.

The applicability of catastrophe theory to emulsion phase inversion was first suggested by Dickinson (4). This suggestion was based on the fact that phase inversion induced by increasing the volume fraction of the dispersed phase displays the qualitative characteristics of the so-called *cusp catastrophe*, one of the elementary catastrophes from Thom's catastrophe theory. The most outstanding characteristic was the occurrence of *hysteresis*, which could not be explained by other theories at that time.

The cusp catastrophe is characterized by only one behavior parameter (S), which should indicate the morphology of the system (i.e., O/W or W/O). Further, there are two control parameters: a *normal factor* (A), which tends to increase or decrease S smoothly and monotonically, and a *splitting factor* (B), which promotes the occurrence of hysteresis. According to Dickinson, the normal factor A is intuitively

FIG. 1. Ball-in-hole analogy to explain hysteresis.

related to the fraction of one of the phases, and the splitting factor B to the concentration of emulsifier. The physical nature of the morphology parameter S remained yet undetermined.

For an emulsion, the appropriate optimization function is the Gibbs free energy of the system. According to the theory of the cusp catastrophe, the Gibbs free energy should be represented by³

$$G(S) = \frac{1}{4}S^4 + \frac{1}{2}BS^2 + AS. \quad [1]$$

On the basis of this equation, hysteresis in emulsion phase inversion can be visualized by means of a “ball-in-hole” analogy (5) (Fig. 1). This shows immediately one of the most important prepositions of the catastrophe theory: the *perfect delay convention*, according to which the system always remains in a local optimum.

A more quantitative approach by means of the catastrophe theory is strongly limited by the yet undetermined nature of the morphology parameter S . Dickinson suggested an aver-

³ There is no uniform notation of the algebra describing elementary catastrophes. We have found no less than four different notations in the literature for the optimizing function characterizing the cusp and butterfly catastrophes:

Cusp	Butterfly	Reference
$1/4 x^4 + 1/2 ax^2 + bx$	$1/6 x^6 + 1/4 ax^4 + 1/3 bx^3 + 1/2 cx^2 + dx$	(9)
$1/4 x^4 - ax - 1/2 bx^2$	$1/6 x^6 - ax - 1/2 bx^2 - 1/3 cx^3 - 1/4 dx^4$	(3)
$s^4 + as^2 + bs$		(4)
$1/4 x^4 + 1/2 cx^2 + dx$	$1/6 x^6 + 1/4 ax^4 + 1/3 bx^3 + 1/2 cx^2 + dx$	(10)
$1/4 S^4 + 1/2 BS^2 + AS$	$1/6 S^6 + 1/4 DS^4 + 1/3 CS^3 + 1/2 BS^2 + AS$	This paper

The notation used in this paper is not identical to either of those found in the literature. Instead, we have combined the best properties of each of these notations according to the following principles: avoiding confusion by minus signs as much as possible, avoiding large factors in the bifurcation set, higher coefficients (C , D) should indicate more complicated behavior than lower coefficients (A , B), and normal and splitting factors from both cusp and butterfly catastrophes should be indicated by the same coefficients. Furthermore, we have used capital coefficients to avoid confusion with the a , b , c , and d parameters in Eqs. [11]–[16].

age degree of curvature of oil and water surfaces as a possible morphology parameter. However, all uncertainty can be avoided by focusing on the bifurcation set, in which behavior parameters are not present.

Our ultimate goal is to develop a model that can predict the fraction dispersed phase at which inversion takes place as a function of relevant formulation and emulsification parameters. We will first compare the elementary algebraic forms for bifurcation sets to experimental data from the literature. Furthermore, we will set up a description for the Gibbs free energy of an emulsion system on the basis of relevant physical parameters and derive catastrophic behavior from that.

EXPERIMENTAL TEST OF THE CATASTROPHE THEORY

(a) Phase Inversion in a Binary Water–Amphiphile System

Comparisons between the cusp catastrophe bifurcation and experimental phase inversion data were done by Smith and Lim (6, 7). In a binary, water/2-butoxyethanol system (6), phase inversion experiments were undertaken to determine ϕ_1 and ϕ_2 , i.e., the volume fractions of amphiphilic phase at which inversion took place, as a function of temperature, close to the critical point. ϕ_1 is the inversion point from Aq/Am (aqueous phase in amphiphilic phase) to Am/Aq, and ϕ_2 is the inversion point from Am/Aq to Aq/Am. From the graphical presentation of the experimental data, $\phi - \phi_c$ could be identified as the normal factor, and $T - T_c$ as the splitting factor, where (ϕ_c, T_c) is the critical point.

The critical temperature T_c was determined by extrapolation of conductivity measurements, and the critical inversion point ϕ_c was disputably set to 0.5, following Ross and Kornbrekke (8), who derive the probability of finding an emulsion in morphology a/b on the basis of a canonical partition function Z . In their analysis, implicit assumptions regarding the morphology of the emulsion are made, which may not be justified in many systems. For example, the partition function Z is given by

$$Z = \sum_{\text{states}} \exp(-(E_0 + \sigma A)/kT) = Z_0 \exp(-\sigma A/kT), \quad [2]$$

where E_0 represents the energy level of the unmixed phases. Indeed, for all states E_0 is equal, so the use of a constant Z_0 is justified; but it is apparently also assumed that A is equal for all states, which is not true. It can however be argued that emulsion states with an extreme value of A do not contribute significantly to Z , such that

$$Z_{a/b} = Z'_0 \sum_{\text{states}} \exp(-\sigma A/kT) \approx Z_0 \exp(-\sigma \bar{A}/kT), \quad [3]$$

which makes the following deductions only approximate.

Another implicit assumption can be found in the relation between the difference in interface ΔA and the volume fraction ϕ :

$$\Delta A = (\alpha + \beta) \phi - \beta, \quad [4]$$

with

$$\alpha = \frac{3(V_a + V_b)}{\bar{R}_a} \text{ and } \beta = \frac{3(V_a + V_b)}{\bar{R}_b}. \quad [5]$$

The above equalities imply a droplet distribution very close to monodisperse, whereas in reality, polydispersity in emulsions can be considerable, especially close to the catastrophic inversion point. Therefore, the above relations are, again, an approximation, allowing at most to say $\phi_c \approx 0.5$. Finally, the whole analysis by Ross and Kornbrekke is disputable, since it assumes phase inversion to be a stochastic process. This assumption is based on observed stochastic phase inversion behavior in their experiments. We believe however that their stochastic observations are not a result of a stochastic nature of the phase inversion process itself, but rather of the stochastic nature of the agitation method employed (shaking by hand).

Instead of setting the critical inversion point to 0.5, ϕ_c can be defined as the common limit of ϕ_1 and ϕ_2 for T approaching T_c . Determining ϕ_c by extrapolation of ϕ_1 and ϕ_2 to $T = T_c$, we find a value of $\phi_c = 0.53$ for the binary water/2-butoxyethanol system.

The singularity set of the cusp catastrophe can be derived from Eq. [1] and the conditions $\partial G / \partial S = 0$ and $\partial^2 G / \partial S^2 = 0$. By eliminating the behavior parameter S , i.e., projecting the singularity set (in $A \times B \times S$ space) onto the control ($A \times B$) space, the bifurcation set is obtained:

$$\left(\frac{A}{2}\right)^2 = -\left(\frac{B}{3}\right)^3. \quad [6]$$

A direct fit of this bifurcation set to the experimental data is not satisfactory (see Fig. 2). The main reason for this is that Eq. [6] requires the cusp to be symmetrical around the axis $A = 0$, i.e., the critical value of the volume fraction, whereas the data points are clearly not located symmetrically around ϕ_c . However, catastrophe theory was successful in fitting the hysteresis width $\Delta\phi = \phi_1 - \phi_2$. On the basis of Eq. [6], it is expected that $A \sim B^{3/2}$. Indeed, $\Delta\phi \sim (T - T_c)^{3/2}$ proved to be a satisfactory fit, although the best fit was $\Delta\phi \sim (T - T_c)^{1.22}$.

In order to fit the experimental data mentioned, a mathematical description of an asymmetrical cusp is required. This can be accounted for by an elementary catastrophe of a higher order, for instance, the butterfly catastrophe (2, 9).

FIG. 2. Cusp and butterfly catastrophe fits on experimental data from a binary water/2-butoxyethanol system (Smith and Lim (6)).

The butterfly catastrophe is characterized by a polynomial optimization function of the sixth order:³

$$G = \frac{1}{6}S^6 + \frac{1}{4}DS^4 + \frac{1}{3}CS^3 + \frac{1}{2}BS^2 + AS. \quad [7]$$

Characteristics of the butterfly catastrophe have been described by various authors (3), also with respect to emulsion phase behavior (1, 10). The butterfly catastrophe can best be understood in terms of a bifurcation set on $A \times B$, with C and D as additional parameters. For $C = 0$ and $D = 0$, the bifurcation set looks like an ordinary cusp. For $C > 0$, the cusp swings to the right, for $C < 0$, to the left. A value of $D > 0$ reduces the asymmetry effect of the C parameter, but does not change the general shape of the bifurcation set. For $D < 0$, more complex bifurcation sets are obtained: two cusps may overlap, creating a so-called pocket. Salager (10) has shown the qualitative similarities between a butterfly catastrophe pocket and a three-phase region in a surfactant/oil/water ternary phase diagram. Since we are only concerned with morphology behavior showing similarities to a single, possibly asymmetric cusp, we can limit ourselves to values of $D \geq 0$.

Following an approach outlined by Poston and Stewart (9), we can derive the bifurcation set of the butterfly catastrophe:

$$A = 4S^5 + 2DS^3 + CS^2 \quad [8a]$$

$$B = -5S^4 - 3DS^2 - 2CS. \quad [8b]$$

Since Eq. [8b] has up to four real roots, it is in theory possible to express the bifurcation set as a set of up to four

explicit functions $A = f(B)$. However, this involves such extensive algebra that the result is not practical for any purpose, including curve fitting. With the Eqs. [8a] and [8b] it is, however, easy to obtain satisfactory fits by trial and error.

Another limitation is necessary: since $D > 0$ only reduces the effect of a nonzero value of C , without changing the general shape of the bifurcation set, we limit ourselves to $D = 0$. This allows us to obtain an explicit expression for the cusp point:

$$S_{\text{cusp}} = -\sqrt[3]{\frac{C}{10}}. \quad [9]$$

The cusp catastrophe equations are such that the cusp point corresponds to $(A, B) = (0, 0)$. This is quite practical for fitting, since normal factor and splitting factor are defined with respect to the critical point, $\phi - \phi_c$ and $T - T_c$, respectively. With the more complex butterfly catastrophe equations, the cusp point no longer corresponds to $(A, B) = (0, 0)$. With the help of Eq. [9], Eqs. [8a] and [8b] can be modified in order to obtain a cusp point $(0, 0)$:

$$A^* = 4S^5 + CS^2 + 14\left(\frac{C}{10}\right)^{5/3} \quad [10a]$$

$$B^* = -5S^4 - 2CS - 25\left(\frac{C}{10}\right)^{4/3}. \quad [10b]$$

We will now fit the relationship $\phi - \phi_c = K_A A^*$ and $T - T_c = K_B B^*$. Since the relationship between A^* and B^* cannot be given explicitly, standard nonlinear curve fit procedures cannot be applied to this problem. We have instead used the following procedure: first, the parameters K_A , K_B , and C were estimated by trial and error, until an apparently reasonable fit was obtained. The temperature was chosen as the independent parameter, and the sum of squares of the differences between calculated and experimental inversion points (volume fractions) was evaluated. Then all three fit parameters were varied stepwise, with decreasing step size, until a minimum sum of squares was reached. It cannot however, be guaranteed that this local minimum is the global minimum sum of squares.

The results are presented in Table 1, and the fitted curves are plotted in Fig. 2, together with the cusp catastrophe fit by Smith and Lim (6). The butterfly catastrophe fit is much better than the cusp catastrophe fit, although still unsatisfactory. As can be seen from Fig. 2, the quality of the fit is much better for the value of $\phi_c = 0.53$, obtained by extrapolation of experimental data, than for $\phi_c = 0.5$, as derived by Ross and Kornbrekke (8). Hysteresis width can also be fitted by the butterfly catastrophe. Since hysteresis width is a symmetrical variable, we can limit ourselves to the case of $C = 0$.

TABLE 1
Values of K_A , K_B , and C Parameters from Butterfly Catastrophe Fits on Experimental Inversion Data

	K_A	K_B	C
Binary system Smith and Lim (6) Fig. 2 $\phi_c = 0.5$	13.9	-0.090	-8.324
Binary system Smith and Lim (6) Fig. 2 $\phi_c = 0.53$	30.5	-0.12	-10.1
Ternary system Lim and Smith (7) Fig. 3 Normal factor ϕ_{water}	0.85	1.00	-36.6
Ternary system Lim and Smith (7) Fig. 4 Normal factor ϕ_{benzene}	2.89	1.78	25.8

Hence we find $A \sim B^{5/4}$, which is very close to the experimental best fit $\Delta\phi \sim (T - T_c)^{1.22}$, much closer than the exponent $\frac{3}{2}$ as predicted by the cusp catastrophe.

(b) Phase Inversion in a Ternary Water/Oil/Emulsifier System

Experimental data which can be employed to test the catastrophe theory are also available for a ternary system. Lim and Smith (7) reconstructed phase inversion data in a water/benzene/ethanol system from Ross and Kornbrekke (8). From a striking similarity between the experimental inversion curve and the cusp-shaped bifurcation lines, the normal factor could be qualitatively related to the water or benzene phase fraction, the splitting factor to the distance from the critical point, which would be in this case the component fraction ethanol. However, these quantities were rejected by Lim and Smith as suitable normal and splitting factors, since they did not form an orthogonal system. Data were transformed into a polar coordinate system in order to obtain parallel tielines, which, according to Lim and Smith, would be a requirement imposed by catastrophe theory. This is not true, however, since an experimental path along a tieline is not necessarily a path of constant splitting factor. At this stage, catastrophe theory is a purely phenomenological model. Normal and splitting factors are identified with physical parameters on the basis of qualitative similarities in behavior. It is hoped that in case a correct fit is obtained, the mathematical relationships between behavior, normal, and splitting factors will reveal the physical relationships between the physical parameters they are associated with. A correct definition of the splitting factor is the definition for which the mathematical description in the catastrophe theory

FIG. 3. Butterfly catastrophe fit on experimental data from a ternary water/benzene/ethanol system (Lim and Smith (7)) using ϕ_{water} as the normal factor.

framework is in agreement with the physical nature of the associated parameter. The splitting factor may well be defined such that the tielines are lines of constant splitting factor. This may be done by a polar coordinate transformation as suggested by Lim and Smith (6), or in this particular case by defining the splitting factor as the fraction ethanol in the aqueous phase. However, there is no indication yet that such a definition will lead to agreement between mathematical and physical relationships. Therefore, we have chosen to define the normal and splitting factor as closely related to the experimental practice as possible: the component fraction water or benzene as normal factor and the component fraction ethanol as splitting factor.

We have performed fits on both $\phi_{\text{water}} - \phi_{\text{water},c} = K_A A^*$ and $\phi_{\text{benzene}} - \phi_{\text{benzene},c} = K_B B^*$ versus $\phi_{\text{ethanol}} - \phi_{\text{ethanol},c} = K_C C^*$. Here, all fractions ϕ represent component fractions. The results of the fits are presented in Table 1 and Figs. 3 and 4. The visual quality of both fits is reasonable, at least much better than a symmetrical fit of the cusp catastrophe. The fit is obviously lacking one important characteristic: the experimental points show one leg to be convex and the other to be concave toward the inside of the cusp. However, the butterfly catastrophe requires both legs to be convex toward the inside of the cusp.⁴ The visual quality of the fit can probably be increased by employing elementary catastrophes

of an even higher order, but only at the cost of introducing more fit parameters whose physical significance becomes more and more obscure.

As for the physical significance of the employed fit parameters K_A , K_B , and C , only the C parameter can be qualitatively interpreted, being related to the HLB of emulsifier. If $\text{HLB} > 7$, O/W morphology will be preferred, and the inversion curve will be skewed to the side of low fraction aqueous phase. If the splitting factor is defined on the basis of the fraction aqueous phase, this will correspond to $C < 0$, hence, $C \sim 7 - \text{HLB}$. If the splitting factor is defined on the basis of the fraction organic phase, $C \sim \text{HLB} - 7$. This is in agreement with Salager (10), who found a relationship between the cubic coefficient from the Gibbs free energy equation of the butterfly catastrophe and the surfactant affinity difference, a parameter incorporating the effect of the HLB of the emulsifier.

(c) Evaluation of Experimental Tests of the Cusp and Butterfly Catastrophes

Although the cusp catastrophe may successfully describe phase inversion phenomena on a qualitative basis, it cannot be employed to fit experimental data. The more sophisticated butterfly catastrophe, which displays under the assumption $D \geq 0$ exactly the same qualitative characteristics as the cusp catastrophe, resulted in visually better fits. Elementary catastrophes of a higher order may improve the quality of the fit. However, for catastrophe theory to be a quantitative, predictive model, it is essential that the fit parameters have

FIG. 4. Butterfly catastrophe fit on experimental data from a ternary water/benzene/ethanol system (Lim and Smith (7)) using ϕ_{benzene} as the normal factor.

⁴ From Eqs. [8a] and [8b] it can be deduced that $dA/dB = -S$. Therefore, the gradient of the bifurcation set changes monotonically and counter-clockwise along the curve. This means that both legs of the bifurcation set are convex toward the inside of the cusp.

a physical significance. Employing elementary catastrophes of a higher order will only lead us away from this goal.

Let us reconsider the essentials of catastrophe behavior and the function of elementary catastrophes in describing this behavior. Catastrophic behavior involves sudden changes in behavior of a system as a result of gradually changing conditions. The number of possible behavior states and the number of control parameters involved determines the complexity of the catastrophe. For the catastrophic phenomena observed in emulsion phase inversion, the relevant behavior is outlined in Fig. 1. A description of catastrophic phase inversion is not necessarily of the exact form of Eq. [1], but it should show the qualitative characteristics as shown in Fig. 1.

Any analytical function can be represented within a certain range with a certain accuracy by a polynomial. The accuracy and applicable range will be better with increasing order of the polynomial, at the cost of the introduction of more coefficients. Likewise, any catastrophic behavior can be represented by an elementary catastrophe of a certain order, with accuracy and applicable range increasing with the order of the elementary catastrophe. If relatively high accuracy is demanded, a suitable elementary catastrophe might be much more complex than the actual underlying physical relationships, resulting in many, often highly correlated parameters of little physical significance. As for the elementary cusp catastrophe, this is the simplest function accounting for the behavior outlined in Fig. 1.

PHYSICAL CONSIDERATIONS ON PHASE INVERSION WITHIN THE FRAMEWORK OF CATASTROPHE THEORY

Instead of trying to find an elementary catastrophe that fits experimental data, we will try to deduce catastrophic behavior from a description of the Gibbs free energy of an emulsion system as a function of a relevant morphology parameter. Following the suggestion of Dickinson (4), we choose the curvature of the interface, defined as the reciprocal radius of curvature of the emulsion droplets. Overbeek *et al.* (11) give a description of the Gibbs free energy per unit volume of a droplet-type emulsion in terms of curvature

$$G^M = \sum n_i \lambda_i + n_d \frac{4\pi a^2}{3} \times \left(\sigma + \frac{2c}{a} + \frac{3kT}{4\pi a^2} f_{w/o}(\phi, a) \right), \quad [11]$$

with

$$f_{w/o}(\phi, a) = \ln \phi - 1 + \phi \left(\frac{4 - 3\phi}{(1 - \phi)^2} \right) - \frac{3}{2} \ln \frac{16a^3}{v_w} \quad [12]$$

for a W/O emulsion. ϕ is the volume fraction aqueous phase, and σ is the interfacial tension at zero curvature (infinite radius of curvature).

These equations are accurate enough to describe microemulsion systems. Since the curvature dependence of the Gibbs free interfacial energy becomes less critical for larger droplets, these equations are certainly applicable to miniemulsions and coarse emulsions.

The first term in Eq. [11] represents the chemical potential of the components of the emulsion. Since this term is related only to the composition of the emulsion, not to its morphology, it will be omitted below. The second term, $(4\pi a^2/3)\sigma$, represents the interfacial energy. The third term, $(4\pi a^2/3)2c/a$, accounts for the bending stress, the curvature dependent interfacial energy, expressed by the bending stress coefficient c . The fourth term in Eq. [11] represents the entropy of the dispersed droplets.

The bending stress coefficient c can be written as

$$c = -b + \frac{d}{a} \quad [13]$$

according to Overbeek (12). The parameters b and d are related to the mean and Gaussian bending elasticity moduli k_c and $\bar{k}_c$. By comparing equations from Overbeek (12) and Barneveld (13), it can be deduced that $b = 2k_c/a_0$ and $d = 2k_c + \bar{k}_c$. Typical values are $b \approx 10^{-12}$ N and $d \approx 10^{-20}$ J, which will be used in our calculations.

Eliminating the number of droplets, Eqs. [11] and [13] result in an expression for the interfacial contribution to the Gibbs free energy of the emulsion system G_{int} :

$$G_{\text{int}} = \phi \left(\frac{\sigma}{a} - \frac{2b}{a^2} + \frac{2d}{a^3} + \frac{3kT}{4\pi a^3} f_{w/o}(\phi, a) \right). \quad [14]$$

Following Overbeek (12), we define the curvature of an O/W emulsion as negative curvature. Hence we obtain

$$G_{\text{int}} = -(1 - \phi) \times \left(\frac{\sigma}{a} + \frac{2b}{a^2} + \frac{2d}{a^3} + \frac{3kT}{4\pi a^3} f_{o/w}(1 - \phi, |a|) \right), \quad [15]$$

with

$$f_{o/w}(1 - \phi, |a|) = \ln(1 - \phi) - 1 + (1 - \phi) \times \left(\frac{3\phi + 1}{\phi^2} \right) - \frac{3}{2} \ln \frac{16|a|^3}{v_o} \quad [16]$$

for an O/W emulsion ($1/a < 0$).

Calculating the G_{int} according to Eq. [14] for $1/a > 0$ and according to Eq. [15] for $1/a < 0$, employing the above

FIG. 5. Variation of the normal factor ϕ at $\sigma = 10^{-5}$ N/m. x axis, $1/a$ from -3×10^8 to 3×10^8 m $^{-1}$; and y axis, G_{int} from -3000 to 5000 J m $^{-3}$.

typical values for b and d parameters, we obtain the results as presented in Figs. 5 and 6. We can see that a system described by Eqs. [14] and [15] may display catastrophic behavior. The volume fraction aqueous phase ϕ can be identified as the normal factor, the interfacial tension σ as the splitting factor. Both are in agreement with Dickinson's suggestions (4), since the interfacial tension is, below the CMC, highly correlated with the surfactant concentration.

Simple catastrophic behavior, as qualitatively described by the cusp catastrophe, is only displayed for $\sigma \leq 10^{-5}$ N/m, a typical value for microemulsions. For higher values of the splitting factor, the minima at positive and negative curvature disappear. At $\sigma \geq 10^{-3}$ N/m, a typical value for coarse emulsions, only a very steep minimum at zero curvature⁵ remains.

The bifurcation set can be derived by solving the equations

$$\frac{dG_{\text{int}}}{d(1/a)} = 0 \quad \text{and} \quad \frac{d^2G_{\text{int}}}{d(1/a)^2} = 0. \quad [17]$$

Neither of the above equations can be solved analytically. The first derivative was evaluated numerically employing the bisection method, the second derivative by means of the Newton–Raphson method. Points of the bifurcation set were obtained by bisection of ϕ at a certain value of σ . The bifurcation set is plotted in Fig. 7 and consists of two smooth lines, enclosing the hysteresis region in which two morphology states are (meta)stable. Unlike the cusp catastrophe, the bifurcation lines continue beyond the critical point, marking out a region in which no emulsion state is metastable, only a state of zero curvature, i.e., two separated phases.

For a closer look at this behavior state of zero curvature, we evaluate G_{int} near $1/a = 0$:

$$\lim_{1/a \rightarrow 0} \frac{\partial G_{\text{int}}}{\partial (1/a)} = \lim_{1/a \rightarrow 0} \frac{\partial^2 G_{\text{int}}}{\partial (1/a)^2} = \phi \sigma. \quad [18]$$

⁵ The model for $G_{\text{M}} = f(1/a)$ employed in this paper only accounts for one explicit value of $1/a$ for the whole emulsion system. Therefore, the “zero curvature state” refers to a state of an actual flat interface, i.e., a state of separated phases. It definitely does not refer to a bicontinuous state with average zero curvature, since $1/a = 0$ leads to $G_{\text{M}} = 0$, which is certainly not the case for a bicontinuous state.

FIG. 6. Variation of the splitting factor σ at $\phi = 0.5$. x axis, $1/a$ from -3×10^8 to 3×10^8 m $^{-1}$; and y axis, G_{int} from -3000 to 5000 J m $^{-3}$.

For $\sigma > 0$ there is always a local minimum at $1/a = 0$. This is understandable, since a system of separate phases ($1/a = 0$) will not form droplets spontaneously, unless $\sigma < 0$. Following the perfect delay convention, the system can never escape from this state, since this minimum, unlike the other minima at positive or negative curvature, will never disappear. This would mean that phase inversion is impossible, because any change from positive to negative curvature or vice versa passes through zero, where the system would remain in a local minimum.

The height of the energy barriers at either side of the zero curvature state decreases dramatically with decreasing σ . As can be seen from Fig. 6, the dip becomes negligibly small with respect to the other minima at $\sigma \leq 10^{-5}$ N/m. It has been suggested by Dickinson (14) that agitation of an emulsion will provide energy to the system to “jump” over a certain energy barrier. Employing this concept, we have compared the height of the energy barriers around $1/a = 0$ to the energy provided by agitation. Under steady-state conditions, the energy supply to the emulsion is equal to the energy dissipation rate ϵ (J/kg s). The system will need a certain amount of energy to escape from the zero curvature state. This energy is supplied by agitation at a more or less constant rate, but it cannot be accumulated over infinite time. The presence of eddies arriving at an element of the interface is felt during a time τ_k , with $\tau_k = (\nu/\epsilon)^{1/2}$ the Kolmogorov time scale. During this time, an amount of $\epsilon \tau_k$ of kinetic energy per unit mass can be supplied to that element. If this amount of energy is less than the amount required for the interface to escape from the zero curvature state, the interface

FIG. 7. Bifurcation set of a system obeying Eqs. [14] and [15].

FIG. 8. Examples of phase inversion paths.

will only deform, and the kinetic energy is soon dissipated with the relaxation of this deformation. If, however, the amount of energy supplied exceeds the height of the energy barriers around the zero curvature state, the interface will break and droplets will be formed. Therefore, the maximum energy barrier that can be overcome can be estimated from the energy supply of one single eddy:

$$\Delta G_{\max} \approx \epsilon \rho \tau_K = \sqrt{\mu \rho \epsilon}. \quad [19]$$

In a well-baffled stirred vessel, at sufficiently high impeller speed, the (average) energy dissipation rate may be obtained from (15)

$$\epsilon = C_1 N^3 d_{\text{imp}}^2, \quad [20]$$

with N the number of impeller revolutions per second and d_{imp} the impeller diameter. C_1 is a constant depending on the geometry of the vessel and impeller, usually in the order of 1.

With $N = 16.7 \text{ s}^{-1}$ (1000 rpm) and $d_{\text{imp}} = 5 \text{ cm}$ we find a typical value of $\epsilon \approx 10 \text{ J/kg s}$. In Fig. 7 we have also indicated the lines for which the minimum at zero curvature is enclosed by energy barriers of at least $\Delta G_{\max}$ as given by Eq. [19], for values of $\epsilon = 1, 10$, and 100 J/kg s .

In Fig. 8 the bifurcation lines are shown, together with the line of a critical energy barrier for $\epsilon = 10 \text{ J/kg s}$. Point P represents a W/O emulsion. Adding aqueous phase to this emulsion, containing a certain concentration of surfactant such that σ remains constant, we follow path $PQRST$. The emulsion will remain W/O until point S is reached, where inversion will occur. The ball-in-hole representation of this process is given in Fig. 9. Going the other way, starting at point T with an O/W emulsion, we follow path $TSRQP$ by adding organic phase. Inversion will now occur at point Q . QS represents the hysteresis width at this specific value of σ .

The influence of the energy barrier around the state of zero curvature becomes clear following the path UVW . We start at point U with a W/O emulsion, agitated such that ϵ

$= 10 \text{ J/kg s}$. Adding aqueous phase, the W/O morphology becomes unstable at point V . Since point V is located above the dotted line, which encloses the region where the energy barrier around the state of zero curvature is high enough to "trap" the system, the emulsion will not invert. Instead, phase separation will occur. This process is illustrated by means of the ball-in-hole analogy in Fig. 9.

EVALUATION OF THE APPLICABILITY OF CATASTROPHE THEORY

We have shown that a description of the Gibbs free energy of an emulsion system as a function of the curvature of the droplets can account qualitatively for all catastrophic phenomena observed with respect to emulsion phase inversion. A physically relevant behavior parameter and normal and splitting factors could be identified. On the basis of this model it is expected that for values of the interfacial tension $\sigma \geq 10^{-3} \text{ N/m}$ the emulsion system will tend to separate, and catastrophic phase inversion cannot occur. This result is not very surprising, since it is generally known that coarse emulsions are not thermodynamically stable. It is, however, surprising that catastrophic phase inversion, with all characteristics of a catastrophe, still occurs in coarse emulsions at $\sigma \geq 10^{-3} \text{ N/m}$. There are two possible explanations for this:

1. The curvature of the interface is not the appropriate behavior parameter to be used in catastrophe theory. There is another, physically relevant behavior parameter that will give rise to catastrophic behavior in the appropriate ranges of normal and splitting factors, i.e., also for coarse emulsions.
2. Catastrophe theory is not applicable to phase inversion in coarse emulsions at all. The observed hysteresis phenomena have another, noncatastrophic, nature.

While we cannot prove that the first explanation is wrong, we can raise two important objections against it. The first objection is that curvature is the very most appropriate behavior parameter. Catastrophe theory requires a continuous parameter to describe discrete morphology behavior. Of all continuous parameters characterizing an emulsion system,

FIG. 9. Ball-in-hole representation of the inversion paths from Fig. 8.

curvature is most directly related to emulsion morphology, provided its sign is defined according to the morphology. A state of zero curvature seems a natural transition state between O/W and W/O morphology. Furthermore, the proposed description of the Gibbs free energy of the emulsion system did show catastrophic behavior, only not in the appropriate range of σ . It is very unlikely that there are two possible behavior parameters giving rise to catastrophic behavior, each in another range of respective normal and splitting factors.

A second objection against the first explanation is that the application of curvature as a behavior parameter in catastrophe theory leads to the conclusion that above a certain value of the interfacial tension emulsions are not thermodynamically stable systems, a generally known fact. It has already been stated by Salager (1) that care has to be taken when treating emulsion phase inversion in a thermodynamic way. Salager assumed that the processes causing an emulsion to break (coalescence) are slow with respect to the processes that govern phase inversion. The observation of catastrophic phenomena and the fact that transitional inversion could be very well described on the basis of equilibrium thermodynamics seemed to justify thermodynamic treatment of catastrophic phase inversion. In case of transitional inversion, the stability of the emulsion before and after phase inversion is comparable. Catastrophic phase inversion, however, involves inversion from a highly unstable morphology to a more stable one. Also, the coalescence processes which cause unstable emulsions to break play a much more important role in catastrophic phase inversion than in transitional inversion. Therefore, thermodynamic treatment might give good results in case of transitional inversion, but is certainly inappropriate to catastrophic inversion.

Assuming that the second explanation is the right one, the question arises which is the nature of the hysteresis phenomena observed. It has been suggested that phase inversion in liquid-liquid systems is governed by coalescence (16). Vaessen and Stein (17) pointed out in the case of catastrophic inversion the appropriate mechanism is dependent on the direction in which inversion is carried out. The key issue here is the influence of the surfactant distribution on the coalescence kinetics. With the surfactant present in one of the phases, Bancroft's rule (18) predicts a preferred morphology. While originally Bancroft's rule was interpreted in terms of preferred curvature of the interface, Traykov and Ivanov (19) have shown that it can also be interpreted in terms of coalescence efficiency. With the surfactant present in the continuous phase, film drainage between droplets is strongly retarded by gradient in surface tension. Such a system will coalesce slowly, and phase inversion will be opposed. With the surfactant present in the dispersed phase, a surface tension gradient will not be formed, since any shortage of surfactant caused by the drainage flow in the film will be immediately compensated by diffusion from the bulk of the droplet. Coalescence will be fast and the system will

easily invert. In case of "slow" coalescence, inversion will take place when the interaction time of the droplets exceeds the drainage time; in case of "fast" coalescence, it is the balance between breakup and coalescence of the droplets that will determine the inversion point. Whenever an emulsion has inverted and the process is reversed, another inversion mechanism will be applicable. Therefore, hysteresis may result from the different mechanisms involved.

A final question that remains is whether catastrophe theory is applicable to microemulsions. On the basis of Eqs. [14] and [15] and Fig. 7, catastrophic behavior is to be expected in the microemulsion range ($\sigma \leq 10^{-5}$ N/m). However, catastrophic behavior is not generally observed regarding microemulsions. For coarse emulsions, the volume fraction ϕ is determined by the bulk formulation of the emulsion system. The droplet size is adapted by means of coalescence and break-up of droplets. Microemulsions are often in equilibrium with excess dispersed phase and may exchange this phase between the droplets and the bulk excess phase in order to minimize the Gibbs free energy of the system. The droplet size in this case is adapted by changing the volume fraction in the emulsion phase, keeping the number of droplets generally constant. Because of this extra degree of freedom, microemulsions may escape from a local minimum in Gibbs free energy by adapting ϕ and end up in a state of global minimum Gibbs free energy. Microemulsions do not therefore obey the perfect delay convention. As a result, catastrophic behavior is not to be expected.

CONCLUSIONS

In this paper, the applicability of catastrophe theory to emulsion phase inversion has been investigated. Two applications have been considered: (i) catastrophe theory as a fitting model for experimental phase inversion data, and (ii) catastrophe theory as a predictive model for phase inversion. In order to investigate applicability, two approaches have been followed: (i) improving the fit quality by applying elementary catastrophes of a higher order, and (ii) building a model describing catastrophic behavior on thermodynamic properties of an emulsion.

As far as the possibilities for fitting are concerned, fit quality can indeed be improved following the first approach. While the cusp catastrophe can only describe qualitative features of catastrophic phase inversion and fit the hysteresis width, the butterfly catastrophe can fit experimental data directly, both in a binary and a ternary system, with reasonable accuracy. Still, the butterfly catastrophe cannot account for all features of the experimental data; in particular the butterfly catastrophe requires both legs of the bifurcation set to be convex toward the inside of the cusp. Accuracy may be improved by applying elementary catastrophes of a higher order, but at the cost of the introduction of more fit parameters. While already the nature of all parameters from the butterfly and even the cusp catastrophe is not yet resolved,

a better fit of catastrophe theory will not result in better understanding of the phase inversion process. Therefore, the first approach will fail in finding a predictive model.

Following the second approach, an expression for the Gibbs free energy of an emulsion system as a function of the curvature of the droplets could be used instead of an elementary algebraic form to describe the qualitative features of catastrophic phase inversion. With the curvature of the droplets as the behavior parameter, the volume fraction of one of the phases could be identified as the normal factor and the interfacial tension as the splitting factor. On the basis of this expression, catastrophic behavior is to be expected in the microemulsion range ($\sigma \leq 10^{-5}$ N/m), but not in the coarse emulsion range ($\sigma \geq 10^{-3}$ N/m). In reality, however, catastrophic phase inversion is observed in coarse emulsions but not in microemulsions.

It was concluded that the assumptions that justified a thermodynamic treatment of transitional inversion are not applicable to catastrophic inversion. Therefore, catastrophe theory cannot be applied to predict phase inversion in coarse emulsions, which should instead be treated on a kinetic basis. Catastrophic behavior in microemulsions is not observed, since these do not obey the perfect delay convention.

Neither the first nor the second approach resulted in a predictive model for catastrophic phase inversion. As an alternative, we believe that kinetic modeling offers good opportunities. On the basis of coalescence and breakup kinetics, hysteresis can already be explained. Currently, we are investigating the possibilities to predict phase inversion from coalescence and breakup kinetics. A paper concerning our promising experiences is in preparation.

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