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Droplet Growth and Transition to Coalescence in Confined Geometries

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Abstract

A thermodynamic theory is developed to predict growth, rearrangement to a close-packed ensemble, and transition to a deformed or coalesced state for droplets in a confined space. For the close-packed configuration, analysis of forced interactions between confined droplets yields analytical criteria for predicting whether droplets will deform, and if they will coalesce. Relevant nondimensional parameters are identified to generalize results in terms of energy barrier maps, and their use for predicting interacting droplet behavior is described.

1. Introduction

When droplets or bubbles interact they may coalesce, deform, or rigidly repel one another. The behavior of small droplets suspended in a liquid, i.e., colloidal dispersions of liquids and emulsions, is an example of such interactions which has been thoroughly investigated¹. Most previous studies have considered dilute suspensions²; more recently progress in dense emulsions has been made³. In many cases only thermal energy (diffusion) drives droplet dynamics, so the droplet motion is random and unconstrained in three-dimensional space. This work considers situations in which droplets are confined and interactions are forced. In the area of dense emulsions⁴ and foams⁵, there has been considerable research into the properties and evolution of related systems, where gravitationally induced drainage plays a role; however, such drainage is not necessarily important in systems where sufficient height/density differences do not exist. The confinement we consider, can occur, for instance, at an interface⁶, within a channel⁷, or within a larger liquid globule⁸ (see Figure 1). The most likely cause of forced interaction in many systems is growth of droplets or bubbles, due to effects of energy and mass transfer. Alternatively, the size of the confinement domain could be reduced. Of interest to us is whether droplets or bubbles will spatially rearrange, whether they will deform, and whether they will coalesce. This is a question of broad practical importance in understanding deposition of thin liquid films^{6,9}, in boiling and condensation^{10,11}, and for droplet interactions in microfluidic devices⁷ including novel micro/nano-reactor systems utilizing double emulsions and liposomes^{8,12}.

In general, two separate volumes of the same phase, separated by a second phase, experience a van der Waals attraction¹³. If the phases are fluid, then it is energetically favorable for the separate volumes to unite, thus minimizing the area of the interface between disparate phases. Hence, coalescence is thermodynamically preferred over the dispersed droplet state in most cases. Coalescence is inhibited by repulsive forces that can be of electrostatic origin in the case of charged surfaces, and may include steric, solvation, thermal fluctuation, protrusion or undulation forces¹³ and possibly lubrication forces¹⁴. Approaches to the prediction of

coalescence can broadly be classified as either quasi-equilibrium or non-equilibrium. In the realm of non-equilibrium descriptions, hydrodynamic forces are frequently important¹⁴. We restrict our attention to the quasi-equilibrium description, which derives primarily from the DLVO theory pioneered by Derjaguin and Landau¹⁵, and Verwey and Overbeek¹⁶. To prevent confusion, we stress that the quasi-equilibrium restriction is applied only to inter-droplet forces, and does not necessarily limit the range of applicable processes driving droplet growth, i.e. energy and mass transfer. The application of a quasi-equilibrium treatment to a portion of a problem is possible when there is a disparity of time scales, as can exist between molecular level and droplet level processes.

We consider the effect of confinement on forced interactions in the case of growing droplets (i.e., cases (a) and (b) in Figure 1), but the modification of our approach to the case of a shrinking domain (i.e., case (c) in Figure 1) is straightforward. We separate our consideration into two distinct stages. First, we consider the case where the droplets are sufficiently far apart and are free to move as they grow in size, so as to minimize the total energy of the ensemble (Figure 1, left column). Second, we analyze droplet behavior upon further growth after the new confined state of the ensemble is established (Figure 1, right column). The droplets now have their center-to-center separation distance fixed, and the only freedom they possess to avoid contact and coalescence upon growth is to undergo deformation. For quasi-equilibrium droplet interactions we answer two basic questions:

1. What conditions are necessary for mobile, undeformed droplets to transition to a close-packed configuration instead of coalescing?
2. What determines whether the subsequent confined growth will force coalescence or produce deformed, but separate, droplets?

By considering the interaction between neighboring droplets, we find a set of general conditions for which coalescence is unlikely due to existence of an energy barrier that is large compared to a thermal energy scale. If unconstrained droplet motion or fluctuations of the surface of constrained droplets are driven by some external field or force, then the use of the thermal energy scale would be inappropriate and the approach must be modified.

The generality of our approach is in providing an analytical framework within which various case-specific interactions can be considered, and thus it carries the advantage of broad applicability. We illustrate it using an important practical example, that of heterogeneously nucleated, conducting droplets (relevant to the electrodeposition of metals), and we present our results in terms of a small set of relevant nondimensional parameters. The example highlights the creation of a simple and general regime-transition-map that can guide prediction or experimental design.

2. General Quasi-Equilibrium Formulation

We begin the presentation of our approach in its most general form, and add restrictions as necessary. In addition to assuming that a quasi-equilibrium description is accurate, we simplify matters by assuming that the droplets are all of the same size, and by considering the behavior of the ensemble as a result of binary interaction between droplets in the domain interior. In other words, our focus is on inter-droplet interaction, not on droplet-boundary interactions, and the propensity of droplets to coalesce under such conditions is analyzed by considering the interaction energy of two identical droplets. Such an approach is equally valid for the entire range of dimensionality depicted in Figure 1 (1-D to 3-D configurations).

2.1 Predicting Coalescence or Rearrangement

First, we consider widely spaced droplets, which may be constrained to a surface as in Figure 1 (b), but are free to move as they grow in size. The total interaction energy, W , between two identical droplets is calculated with respect to the reference state of spherical droplets of the same volume V at infinite separation. In the first stage of analysis, deformation is not considered and the total interaction energy W is the work needed to reversibly reduce the separation distance from infinity to finite D . As a consequence of the attractive van der Waals forces, W has its global minimum when $D = 0$; however, depending upon the other forces between the droplets, W may decrease monotonically with D , or it may possess a primary maximum, and sometimes a secondary minimum, as shown in Figure 2. The energy barrier preventing coalescence, ΔW_b , is the difference between the energy of the primary maximum and the secondary minimum, or, if there is no secondary minimum, simply the maximum energy¹⁶. If there is no maximum then there is no barrier and the droplets will coalesce. Having determined ΔW_b for a particular case, non-coalescence leading to droplet rearrangement is expected when $\Delta W_b/(k_b T) \gg 1$, where k_b is the Boltzmann constant and T is the temperature. Typically ΔW_b increases as droplet radius R increases; therefore, our approach predicts repeated droplet coalescence until critically sized droplets are formed; thereafter rearrangement occurs.

If the droplets continue to grow and rearrange in a bounded space without coalescing, they will eventually achieve a confined state where each droplet is surrounded by neighbors, or by a domain boundary, as depicted in Figure 1 (right). Thereafter, further rearrangement is no longer possible and the distance between the droplet centers, L , does not change appreciably. Continued growth must lead either to deformation or decreased interface separation distance, D , eventually resulting in coalescence.

2.2 Prediction of coalescence or deformation

One of our goals is to determine, for the close-packed state, when droplet interface deformation becomes energetically preferred over radially-uniform growth that brings the droplet surfaces closer together. Furthermore, we determine when such deformation delays or prevents coalescence. Following a previously established approach¹⁷⁻¹⁹, we simplify the treatment by approximating the shape of the deformed droplets as the spherical segments depicted in Figure 3. It has been shown that the truncated sphere approximation depicted in Figure 3 provides accurate results for interaction energy calculations when compared to numerical calculations in which droplet shapes are found using an augmented Laplace equation of capillarity²⁰. This comparison, although necessarily performed for a specific set of interaction energy parameters and a limited droplet size range (1-10 μm), provides confidence in the broad validity of the truncated sphere approximation.

For deformed droplets, the total interaction energy between two droplets, W , depends not only upon the minimum separation distance D , but also on droplet shapes. For close-packed droplets approximated as truncated spheres as in Figure 3, the interface separation distance is a function of droplet radius: $D = L - 2R$. Due to the approximation of the shape as a truncated sphere, for a given L , we can express both volume and interaction energy as functions of a and R . We want to find for each volume the extrema of the interaction energy function. This is a problem of finding the extrema of a function subject to a constraint, i.e., a Lagrange multiplier problem²¹. This is mathematically expressed by a statement that the gradients of the interaction energy and the volume constraint functions are parallel, i.e., $\nabla W = \lambda \nabla V$, which is equivalent to a statement that the vector product of the gradients is zero: $\nabla W \times \nabla V = 0$. Expanding the latter expression yields that the local extrema (minima or maxima) of the interaction energy for a given volume occur for combinations of a and R that satisfy

$$\frac{\partial V(a,R)}{\partial a} \frac{\partial W(a,R)}{\partial R} = \frac{\partial V(a,R)}{\partial R} \frac{\partial W(a,R)}{\partial a} \quad (1)$$

For the truncated sphere approximation in Figure 3, the volume is given by

$$V = \frac{\pi}{3} (2a^3 + 3a^2R - R^3) \quad (2)$$

The transition to deformed growth is expected to occur where, starting from a spherical shape, the increase of interaction energy with increasing volume is the same for deformed and undeformed growth: beyond the transition point, the rate of this increase must be lower for the growth accompanied by interface deformation. If such a transition to deformation is predicted, then a determination of subsequent coalescence following deformed growth is again made by comparing the magnitude of an energy barrier to the scale of thermal energy.

The interaction energy for deformed growth depends upon more than one variable, and thus the energy barrier is not as readily identified as in the case of growing spherical droplets. Identifying the energy barrier for the general case is made simpler by consideration of the following. At relatively small volumes, and therefore large separation D , inter-droplet forces are negligible and interaction energy is entirely due to deformation. Hence, at small volumes the undeformed state is energetically preferred. At the other extreme, of relatively large volumes, a state of vanishing separation distance becomes possible. Here the undeformed state is again preferred, albeit for a different reason. The van der Waals attraction makes $W \rightarrow -\infty$ as $D \rightarrow 0$. For fixed droplet positions, a separation distance $D = 0$ first becomes possible if the growing droplet is in the undeformed state with droplet radius a equal to half the center-to-

center separation L , i.e., $V = \frac{\pi}{6} L^3$. Therefore, the undeformed state must again become the lowest energy state as $V \rightarrow \frac{\pi}{6} L^3$. A consequence of these two observations is that when there is a regime for which the deformed shape is energetically preferred, it is bounded. For such cases, we define the critical volume, V_c , as the volume above which the undeformed state regains its globally minimal status. The energy barrier, ΔW_b , is the magnitude of the maximum change in energy along a constant volume path from the lowest energy deformed state at $V = V_c$ to the undeformed state at $V = V_c$. It is found by determining the difference between the local interaction energy extrema at the critical volume V_c . If $\Delta W_b \gg k_b T$, then deformed growth can be expected to continue until some other heretofore unconsidered energy becomes important. Otherwise, deformed growth is expected to be at most a transient phenomenon followed by a restoration of undeformed growth and subsequent coalescence.

2.3 Application of the Derjaguin Approximation

Next we begin a gradual departure from generality, dividing the interaction energy into two components: the DLVO energy, W_{VE} , and the deformation energy, W_D . Using a general interaction energy per unit area between planar surfaces, $f(D)$, the DLVO energy for truncated spheres is given through the Derjaguin approximation¹⁹:

$$W_{VE}(a,R) \approx \pi(a^2 - R^2) f(D) + \pi a \int_D^\infty f(H) dH \quad (3)$$

Equation (3) is valid when the separation distance is much smaller than the droplet radius, $D \ll a$, and the deformation is slight, $(a - R)/a \ll 1$. Equation (3) does not necessarily restrict the type of interactions that can be considered, as these are specified through the choice of interaction energies, $f(D)$. Note that the undeformed droplet interaction energy is obtained by letting $a = R$ in Eq. (3). Use of Eq. (3) and a description of deformation energy will allow us

to develop a criterion which determines a critical droplet radius R^* (or separation D^* equivalently). The critical droplet radius, R^* , should be the radius for which the rates of interaction energy increase due to undeformed growth or deformed growth are the same, starting from the undeformed state (a first derivative condition). We show that this condition is not sufficient, and we must apply a second derivative condition, i.e., determine when the *rate of change of the increase* of the interaction energy with respect to volume is also the same whether the growth mode is deformed or undeformed. It is the second derivative condition that defines the transition point from undeformed to deformed growth.

Using the Derjaguin approximation, Eq. (3), the rate of change of DLVO energy, W_{VE} , with respect to volume for *incipient deformed growth* is found by differentiation to be

$\frac{f(D^*)}{2R^*} + \frac{1}{4R^{*2}} \int_{D^*}^{\infty} f(H) dH$. This happens to be identical to the expression found for the rate of change of DLVO energy with respect to volume for undeformed growth at $R = R^*$. In other words, *starting from the undeformed state*, continued growth as undeformed spheres, or a transition to deformed growth with constant center-to-center separation, causes the DLVO energy, W_{VE} , to increase at the same rate, regardless of droplet size and separation distance.

The deformation energy, W_D , is always zero for the undeformed configuration, hence the rate of change of deformation energy with respect to volume for undeformed growth is always zero. And because the deformation energy is at a minimum in the undeformed state, the rate of change of W_D with respect to volume for *incipient deformed growth* is also zero. So for both components of the interaction energy we find the rate of change of interaction energies with respect to volume is the same for deformed and undeformed growth *starting from the undeformed state*. An implication of these results is that comparison of rates of interaction energy increase for deformed and undeformed growth cannot predict the transition between the growth modes; hence the second derivatives are needed.

The required expressions for deformed and undeformed DLVO energies are

$$\begin{aligned} \frac{d^2}{dV^2}(W_{VE})_{\text{def}} &\equiv \left[\frac{d}{da} \left(\frac{dW_{VE}}{da} \frac{da}{dV} \right) \left(\frac{da}{dV} \right) \right]_{a=R^*} \bigg|_{a=R^*}^{\infty} \\ &= -\frac{1}{16\pi R^{*5}} \left[R^* f(D^*) + \frac{3}{2} \int_{D^*}^{\infty} f(H) dH \right] \end{aligned} \quad (4)$$

and

$$\begin{aligned} \frac{d^2}{dV^2}(W_{VE})_{\text{un}} &\equiv \left[\frac{d}{dR} \left(\frac{dW_{VE}}{dR} \frac{dR}{dV} \right) \left(\frac{dR}{dV} \right) \right]_{R=R^*} \bigg|_{R=R^*}^{\infty} \\ &= -\frac{1}{16\pi R^{*5}} \left[4R^{*2} f'(D^*) + 2 \int_{D^*}^{\infty} f(H) dH \right] \end{aligned} \quad (5)$$

We predict a transition to deformed growth when $\frac{d^2}{dV^2}(W_D + W_{VE})_{\text{def}} = \frac{d^2}{dV^2}(W_{VE})_{\text{un}}$. For uniform surface tension, σ , the deformation energy is due to the increase in surface area:

$W_D = 2\pi\sigma \left[3a^2 + 2aR - R^2 - (4a^3 + 6a^2R - 2R^3)^{\frac{2}{3}} \right]$. The required second derivative is given by

$$\frac{d^2}{dV^2}(W_D)_{\text{def}} = \frac{\sigma}{4\pi R^{*4}} \quad (6)$$

Using Eqs. (4)-(6), the second derivative condition results in a growth mode transition criterion:

$$\tau(D^*) = \left[\sigma - f(D^*)/4 - R^* f'(D^*) + (8R^*)^{-1} \int_{D^*}^{\infty} f(H) dH \right] = 0 \quad (7)$$

The transition criterion is satisfied where Eq. (7) has real roots. For a given combination of interaction energy and spatial confinement parameters, i.e. the choice of f and droplet center-to-center distance L , deformation is not expected to occur when Eq. (7) has no real roots, and confined droplets grow until coalescence. Alternatively, Eq. (7) can have one or two real roots; this is the situation when deformation is energetically preferred, and a subsequent coalescence occurs if the magnitude of the appropriately determined energy barrier is less than thermal energy scale. Thus, the critical locus of parameters that bounds the parameter space defining undeformed droplet growth occurs where the minimum of $\tau(D^*)$ is zero, i.e., Eq. (7) has a single real root:

$$\tau(D^*) = 0 \text{ and } \frac{\partial \tau(D^*)}{\partial D^*} = 0 \quad (8)$$

It is worth noting the generality of this result, as Eqs. (7) and (8) allow one to predict transition for an arbitrary interaction function f depending on the problem in hand.

3. Example: Heterogeneously Nucleated Conducting Droplets

As an example to elucidate application of the described methodology, we consider the case of an electrically conducting, non-wetting condensate growing on a planar, electrically conducting substrate, both of which are submerged in an ionic solution. The motivation for this choice is an interest in the process of electrodeposition of mercury⁶. The extent of the conducting substrate provides the frame for droplet in-plane spatial confinement, as in Figure 1 (b), and it maintains the conducting droplets at the same electric potential, Φ_w . For non-wetting droplets, the substrate is sufficiently far from the interaction zone of the droplets so that its effect on interaction energies can be neglected. We consider an interaction energy due to van der Waals attraction and electrostatic repulsion for the case of a $z:z$ electrolyte with bulk molar ion concentrations c_b . The van der Waals interaction energy (per unit area) between planar surfaces, W_v'' , is calculated using the assumptions of Hamaker²², namely pairwise additivity, non-retardation, and no screening: $W_v''(D) = -A_H / (12\pi D^2)$. The Hamaker constant A_H depends upon the composition of the droplets and solution¹³. The electrostatic interaction energy between planar surfaces, W_e'' , is calculated using considerable simplification^{13,23,24}. Specifically, Guoy-Chapman theory and the superposition, or “weak overlap,” approximation are invoked. The resulting expression is $W_e''(D) = 64\gamma^2 R_u T c_b \lambda_D \exp(-D/\lambda_D)$ where $\lambda_D = \sqrt{\epsilon_r \epsilon_0 R_u T / (2c_b z^2 F^2)}$ is the Debye length, $\gamma = \tanh[zF\Phi_w / (4R_u T)]$ is a droplet potential dependent factor that varies between zero and one, F is Faraday's constant, R_u is the universal gas constant, and $\epsilon_r \epsilon_0$ is the dielectric constant of the solution (treated as uniform).

3.1 Predicting Coalescence or Rearrangement

Using the expressions for van der Waals and electrostatic interaction energies per unit area for planar surfaces in the Derjaguin approximation of interaction energy with no deformation, i.e. Eq. (3) with $a = R$ and $f = W_v'' + W_e''$, and then nondimensionalizing, we obtain an expression for the dimensionless DLVO energy for identical spheres:

$$W_{VE}^* = W_{VE} (zF)^2 / \left[16\pi R \epsilon_r \epsilon_0 (R_u T \gamma)^2 \right] = -\kappa_c / \bar{D} + 2 \exp(-\bar{D}) \quad (9)$$

In Eq. (9), the Debye length λ_D has been used to make the separation distance D nondimensional, i.e., $\bar{D} = D/\lambda_D$, and the behavior of $W_{VE}^*(\bar{D})$ can be seen to depend upon only a single parameter: $\kappa_c \equiv A_H (zF)^2 / [192\pi\epsilon_r\epsilon_0\lambda_D (\gamma R_u T)^2]$. Curves of W_{VE}^* are plotted in Figure 2 for three choices of κ_c : $\kappa_c = 0.6$, $\kappa_c = 8/\exp(2) \approx 1.08$, and $\kappa_c = 1.5$. For $\kappa_c \geq 8/\exp(2)$ we find that there is no energy maximum and hence no energy barrier: the droplets will coalesce. For $\kappa_c < 8/\exp(2)$ there is a barrier, and its magnitude is found by first determining the separation

distances $\bar{D}$ for the maximum and secondary minimum, i.e., $\bar{D}: \frac{dW_{VE}^*}{d\bar{D}} = 0$ and $\frac{d^2W_{VE}^*}{d\bar{D}^2} < 0$ or $\frac{d^2W_{VE}^*}{d\bar{D}^2} > 0$, respectively. The magnitude of the difference in interaction energies at these two $\bar{D}$ values is the dimensionless energy barrier to droplet coalescence, ΔW_b^* , and it is plotted in Figure 4.

In practice, having determined, for a particular case, the value of ΔW_b^* , $\Delta W_b/(k_b T)$ is found by multiplication by $16\pi\epsilon_r\epsilon_0 R k_b T \gamma^2 / (ze)^2$, where e is the elementary charge. Then, non-coalescence leading to droplet rearrangement on the substrate is predicted when $\Delta W_b/(k_b T) \gg 1$. For closely spaced nucleation sites, repeated droplet coalescence is predicted until larger, critically sized droplets are formed, with radii $R \geq (ze)^2 / (\Delta W_b^* 16\pi\epsilon_r\epsilon_0 k_b T \gamma^2)$.

3.2 Predicting Deformation

Now we turn our attention to the confined, non-coalescing droplets, which, upon rearrangement have assumed a close-packed configuration with fixed center-to-center separation distance L . In our example case, the criterion for transition from undeformed growth to deformed growth is found by substituting $f = W_v'' + W_e''$ into Eq. (7) and using the criteria set by Eq. (8). The resulting nondimensional transition function is

$$\bar{\tau}(\bar{D}^*) = \frac{\tau(\bar{D}^*)}{\sigma} = \left[\begin{aligned} &1 + \frac{\kappa_e \Lambda}{\bar{D}^3} - \frac{\kappa_e \kappa_c^2}{4\bar{D}^* (\Lambda - \kappa_e \bar{D}^*)} - \frac{3\kappa_e \kappa_c}{4\bar{D}^{*2}} \\ &- \left(\frac{\kappa_e}{2} + \Lambda - \kappa_e \bar{D}^* - \frac{\kappa_c^2}{2(\Lambda - \kappa_e \bar{D}^*)} \right) \exp(-\bar{D}^*) \end{aligned} \right] = 0 \quad (10)$$

The nondimensional transition function in Eq. (10) depends on only three nondimensional parameters. They are $\kappa_e = 16\epsilon_r\epsilon_0 (R_u T \gamma)^2 / [\sigma \lambda_d (zF)^2]$, $\Lambda = 64c_b R_u T \gamma^2 L / \sigma$, and κ_c , which was previously defined. A transition to deformed growth is only predicted for combinations of these parameters such that Eq. (10) has real roots. We limit consideration to $\kappa_e < 1$, where we have found the results to be independent of κ_e . This is a practical limitation, as, for aqueous solutions at room temperature, $\kappa_e \leq 3 \times 10^{-15} [\text{N}] / (\sigma \lambda_D)$. If Eq. (10) has no real roots, then growth will be via undeformed states and coalescence is expected. When Eq. (10) has two real roots, deformed growth is expected, and predictions of non-coalescence require an assessment of the energy barrier as follows.

3.3 Determination of the Energy Barrier for Confined Droplets

The dimensionless total interaction energy, including deformed growth, and scaled using a deformation energy scale, $\bar{W} = W / (2\pi\sigma\lambda_d^2)$, is given by

$$\begin{aligned} \bar{W} \approx & \left(\bar{a}^2 - \bar{R}^2 \right) \left[-\frac{1}{2} \frac{\kappa_e \kappa_c}{\bar{D}} + \kappa_e \exp(-\bar{D}) \right] + \left[3\bar{a}^2 + 2\bar{a}\bar{R} - \bar{R}^2 - \left(4\bar{a}^3 + 6\bar{a}^2\bar{R} - 2\bar{R}^3 \right)^{\frac{2}{3}} \right] \\ & + \bar{a} \left[-\frac{1}{2} \frac{\kappa_e \kappa_c}{\bar{D}} + \kappa_e \exp(-\bar{D}) \right] \end{aligned} \quad (11)$$

The bars over the various lengths in Eq. (11) indicate that they have been made dimensionless using the Debye length, e.g., $\bar{R} = R/\lambda_D$.

Figures 5 and 6 are used to illustrate the procedure for the determination of the magnitude of the dimensionless energy barrier to coalescence in the deformed growth stage, $\Delta\bar{W}$.

Point **a** in Figures 5 and 6 corresponds to one of the roots of the transition function, Eq. (10). For growing droplets, as the volume exceeds that corresponding to point **a** in Figures 5 and 6, deformation becomes energetically preferred, and states along the local minimum energy curve (**a,b,f**) are more probable than states along the undeformed growth curve (**a,h,d,e**). Point **h** in Figures 5 and 6 corresponds to the second root of Eq. (10). The energy barrier magnitude, $\Delta\bar{W}_b$, is determined by first finding the crossover volume, V_c , i.e., the volume above which the undeformed state regains its status as energetically preferable. In Figures 5 and 6 this crossover volume is that associated with points **b**, **c**, and **d**. The magnitude of the energy barrier, $\Delta\bar{W}_b$, is the change in energy along a path of constant volume, $\bar{V} = V_c$ between the path arrived at the following energetically preferred deformed growth (**b**) and the non-deformed state (**d**). If the *dimensional* energy barrier magnitude, ΔW_b , is of the order of $k_b T$ or smaller, then it is likely that the droplets will not stay in the deformed “valley”. If instead the barrier is much larger than $k_b T$, deformed growth can be expected to continue. Therefore, noncoalescence requires $\Delta W_b > k_b T$, so, for nonzero $\Delta\bar{W}_b$ a prediction of coalescence or non-deformed growth depends also on $k_b T / (2\pi\sigma\lambda_D^2)$.

Figure 7 shows a contour plot of $\Delta\bar{W}_b$ valid for $\kappa_e < 1$. Under this limitation, the solutions to the transition criterion, Eq. (8), are the combinations of κ_c and Λ that are represented in Figure 7 by the zero energy barrier contour. For combinations of κ_c and Λ above and to the left of this contour, Eq. (10) has two real roots, so deformed growth is expected, and predictions of non-coalescence require consideration of the energy barrier. Figure 7 presents the summary of the analysis in which the relevant energy barrier is found for each combination of parameters.

4. Conclusion

We have presented a method for determining the deformation and coalescence behavior of droplets growing in a confined domain. The method is relatively general, with details encoded in the selection of the specific interaction energy function. Two simplifications used in the derivation may provide fertile ground for further research: the assumption of identically sized droplets, and the neglect of deformation when predicting rearrangement or coalescence. The general approach we utilize, which consists of calculation of binary interaction energies, determination of the appropriate energy barrier to coalescence, and its comparison to a thermal energy scale could be adapted to both cases. The problems of increased complexity, in which the above assumptions are relaxed, are beyond the scope of this manuscript, and we only provide a brief discussion of where one would expect the consideration of non-identical droplet sizes might lead. The interaction of differently sized droplets should add the possibility of multiple possible trajectories for any given ensemble. For example, starting from four equally sized droplets, they could coalesce to form two equally sized droplets, or to form two droplets with one having a three times greater volume than the other. Yet, this divergence of possible paths is somewhat limited since the energy barrier to coalescence used to predict rearrangement increases with droplet size. Noting that, under the Derjaguin approximation, interaction energies for differently sized spheres are the same as the interaction energies for identical droplets whose radii are given by the harmonic mean of the disparately sized droplets' radii¹³, a droplet is more likely to coalesce with another smaller droplet than with a larger one. Therefore, an ensemble of droplets is more likely to evolve into a state of similarly sized droplets, rather than a state with great variation in droplet sizes. This observation suggests that our assumption of identically sized droplets is not as limiting as it may appear at first look.

In our derivation, we have developed a criterion for transition to deformed confined growth in the case of uniform surface tension and applicability of the Derjaguin approximation. Furthermore, we have demonstrated the use of our method for the example of conducting droplets growing on a planar substrate, highlighting the value of appropriate nondimensionalization and the resulting energy barrier maps. With such maps, an experimentalist can rapidly determine the necessary conditions for observing rearrangement, deformation, and coalescence behavior of a growing dispersed condensed phase in confined geometries.

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References

1. Berkman, S.; Egloff, G. Emulsions and Foams. Reinhold Publishing Corp.; New York, NY: 1941.
2. Dukhin SS, Sjoblom J, Wasan DT, Saether O. Colloid Surface A 2001;180:223–234.
3. Deminiere B, Colin A, Leal-Calderon F, Muzy JF, Bibette J. Phys Rev Lett 1999;82:229–232.
4. Princen HM. Langmuir 1986;2:519–524.
5. Bhakta A, Ruckenstein E. J Colloid Interf Sci 1997;191:184–201.
6. Mauzeroll J, Hueske EA, Bard AJ. Anal Chem 2003;75:3880–3889. [PubMed: 14572057]
7. Chen DL, Gerdt CJ, Ismagilov RF. J Am Chem Soc 2005;127:9672–9673. [PubMed: 15998056]
8. Okushima S, Nisisako T, Torii T, Higuchi T. Langmuir 2004;20:9905–9908. [PubMed: 15518471]
9. Reddy KRC, Turcu F, Schulte A, Kayastha AM, Schuhmann W. Anal Chem 2005;77
10. Juntao Z, Raj MM. J Heat Transf 2005;127:684–691.
11. Beysens D, Knobler CM. Phys Rev Lett 1986;57:1433–1436. [PubMed: 10033448]
12. Tresset G, Takeuchi S. Anal Chem 2005;77:2795–2801. [PubMed: 15859595]
13. Israelachvili, J. Intermolecular and Surface Forces. 2nd. Academic Press; San Diego, CA: 1992.
14. Neitzel GP, Dell'aversana P. Annu Rev Fluid Mech 2002;34:267–289.
15. Derjaguin BV, Landau L. Acta Physicochim URSS 1941;14:633–662.
16. Verwey, EJW.; Overbeek, JTG. Theory of the Stability of Lyophobic Colloids. Elsevier; New York, NY: 1948.
17. Denkov ND, Kralchevsky PA, Ivanov IB, Vassiliev CS. J Colloid Interf Sci 1991;143:157–173.
18. Denkov ND, Petsev DN, Danov KD. Phys Rev Lett 1993;71:3226–3229. [PubMed: 10054889]
19. Danov KD, Petsev DN, Denkov ND, Borwankar R. J Chem Phys 1993;99:7179–7189.
20. Denkov ND, Petsev DN, Danov KD. J Colloid Interf Sci 1995;176:189–200.
21. Amatore C, Szunerits S, Thouin L, Warkocz JS. J Electroanal Chem 2001;500:62–70.
22. Hamaker HC. Physica 1937;IV:1058–1072.
23. Derjaguin, BV.; Churaev, NV.; Muller, VM. Surface Forces. Consultants Bureau; New York, NY: 1987.
24. Probstein, RF. Physicochemical Hydrodynamics: An Introduction. 2nd. John Wiley & Sons; New York, NY: 1994.

Figure 1.

Examples of transitions from interaction of spherical droplets due to random, unconstrained motion (left) to forced interaction due to confinement (right). The schematics represent forced interaction due to growth in a 1-D channel (a), growth on a 2-D interface (b), and a shrinking 3-D domain (c).

Figure 2.

Plot of dimensionless interaction energy, W_{VE}^* , as a function of normalized separation distance, $\bar{D}$, for identical, equipotential spheres in an electrolyte. The forces leading to interaction energies are van der Waals and electrostatic, and are calculated using the Derjaguin approximation and Guoy-Chapman theory, as explained in section 3, where the figure nomenclature is also explained. All combinations of physical parameters are described through the variation of a single nondimensional parameter, κ_c . The curve for $\kappa_c = 0.6$ exhibits a primary maximum and secondary minimum: the difference in the corresponding interaction energies defines the nondimensional energy barrier to coalescence.

Figure 3. Geometry for calculation of interaction energy between two deforming droplets. The deformed droplet shape is approximated by a spherical segment.

Figure 4. Nondimensional energy barrier preventing coalescence of identical equipotential spherical droplets (non-coalescence is predicted when $\Delta W_b \gg k_b T$).

Figure 5.

Nondimensional interaction energy surface $W(\bar{V}, \bar{R}/\bar{a})$ for the example case of equipotential conducting droplets growing on a substrate. Three nondimensional parameters specify conditions: the surface shown is for $\kappa_e = 0.1$, $\kappa_c = 0.8$, and $\Lambda = 100$. The nondimensional volume $\bar{V}$ is obtained by normalizing with the volume of an undeformed droplet at zero separation distance (i.e., $V : a = R = L/2$). Also shown are the local minimum energy curve (heavy line **a,b,f**), the local maximum energy curve (dashed line **h,c**), and the interaction energy curve for undeformed droplets (thin line **a,h,d,e**).

Figure 6.

Projection of three curves on the nondimensional interaction energy surface from the case depicted in Figure 5, onto the undeformed plane, $\bar{R}/\bar{a} = 1$. The points **a-f** correspond to the same points in Figure 5. Points **b**, **c**, and **d** lie on a curve of constant $\bar{V} = \bar{V}_c$ for which the interaction energy for the local minimum (**b**) and the undeformed state (**d**) are the same. The energy barrier $\Delta \bar{W}_b$ is the relative height of the interaction energy of point **c** to the interaction energy of point **b** or **d**. It is used to find $\Delta W_b/(k_b T)$. If $\Delta W_b/(k_b T) \ll 1$, then growth along the deformed path towards point **f** and beyond is predicted; otherwise, a return to the energetically favored undeformed growth is predicted, leading to coalescence.

Figure 7.

Contours of the nondimensional energy barrier, $\Delta\bar{W}_b$, which inhibits coalescence of charged, deformable, confined droplets. For $\kappa_e < 1$, $\Delta\bar{W}_b$ is a function of κ_c and Λ (shown on a log scale). The contour of $\Delta\bar{W}_b = 0$ is the solution of Eq. (10), and coalescence is predicted for combinations of κ_c and Λ below and to the right of this contour. Other combinations of κ_c and Λ , require comparing $(2\pi\sigma\lambda_D^2) \Delta\bar{W}_b$ to k_bT to make a determination of whether coalescence is likely to occur.