

A simple model of the formation of hollow particles by water extraction from colloidal droplets

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A recent study [1] demonstrated how hollow ceramic particles can be produced by a novel sol–gel process [2]. Briefly, a nanometre-sized oxide powder is dispersed in water to form an aqueous sol. This is then mixed with an organic liquid, to produce an emulsion of micrometre-sized colloidal droplets. A water-extracting alcohol is then added to the mixture. Water diffuses out of each droplet and is replaced by alcohol, and the ratio of sol to water concentrations increases, most rapidly in the outer regions of the original droplets. The sol undergoes a gelation transition, which is initiated in these regions, forming a hollow gelatinous shell. A sequence of filtration, drying and calcination of the microcapsules then produces hollow ceramic particles. These are suitable for a number of applications [1] where a material with a low density, low thermal conductivity or low dielectric constant is required. The sol–gel method allows better control over the size distribution of the powder product than some other methods.

In [1] the thickness of the shells was related to the initial sol concentration in water using a simple treatment of the diffusion of water out of the droplets. The model correctly accounted for the tendency to produce denser particles as the initial sol concentration is increased, for reasonably concentrated initial sols. However, for very dilute sols the opposite behaviour is seen, such that denser particles result from more dilute concentrations, and this was not accounted for by the model. In this letter, a simple interpretation of the complete set of observations is offered. The main difference compared to the earlier treatment [1] is that the diffusion of the sol particles is also described, and this accounts for the behaviour. The same criterion for gelation is used, namely that it occurs when the sol-to-water ratio reaches a critical value. The position where this occurs, and hence the geometry of the product, is determined by a competition between water and sol diffusion.

We consider a spherical colloidal droplet of initial radius r_0 suspended in a water-extracting medium, and follow its evolution. The mass concentration of water w changes according to a diffusion equation:

$$\frac{\delta w}{\delta t} = D_w \nabla^2 w \quad (1)$$

with an initial condition of $w = w_0$ for $r \leq r_0$, and $w = 0$ elsewhere; and subject to the boundary conditions $\delta w / \delta r$ at $r = 0$ and ∞ . D_w is the water diffusion coefficient and w_0 the initial water concentration within the droplet. An analogous equation with a diffusion coefficient D_s describes the evolution of the sol particle concentration s . Diffusion of sol particles is slower than that of water molecules, so $D_s < D_w$. The initial sol concentration is s_0 within the droplet and zero outside. It is a simple matter to solve these two diffusion problems numerically, using standard methods [3]. In doing so, it is possible to monitor the ratio of sol to water concentrations $c = s/w$. The criterion for gelation is that this ratio should reach a critical value c_{crit} .

It is more convenient to work with dimensionless equations, and so the substitutions $w' = w/w_0$, $r' = r/r_0$ and $t' = t/\tau$ are made, with τ a timescale. Equation 1 becomes:

$$\frac{\delta w'}{\delta t'} = D'_w \nabla'^2 w' \quad (2)$$

with $D'_w = D_w \tau / r_0^2$. The initial condition becomes $w' = 1$ for $r' \leq 1$ and zero otherwise. The sol diffusion equation is treated similarly, but with the substitution $s' = s/(w_0 c_{\text{crit}})$ and the introduction of $D'_s = D_s \tau / r_0^2$. This is so that the initial profile is $s' = c_{\text{init}} / c_{\text{crit}}$ for $r' \leq 1$ and zero otherwise (with $c_{\text{init}} = s_0 / w_0$), and also so that the gelation criterion becomes $c' = s' / w' = c / c_{\text{crit}} = 1$.

Example radial profiles of w' , c' and s' are shown in Fig. 1, for $t = 10$ and 70 ms after the start of extraction. Diffusion coefficients $D_w = 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $D_s = 0.05 D_w$ have been used, together with $r_0 = 10 \mu\text{m}$ and $c_{\text{init}} / c_{\text{crit}} = 0.5$. The diffusion coefficients are assumed to be independent of mixture composition. The gelation condition is first satisfied at $t = t_{\text{gel}} \approx 79$ ms at $r' = r_{\text{gel}} / r_0 \approx 0.87$. This can, to a first approximation, be taken to signal the formation of a gelatinous membrane at this radius. However, a thin membrane would have little strength and would tend to distort, so a more acceptable criterion for membrane formation would be to demand that the gelation condition $c \geq c_{\text{crit}}$ is satisfied within a shell of a given thickness. A critical thickness of $0.1 \mu\text{m}$ has been used: little difference in the calculations of particle geometry arises from this modified membrane formation criterion (unless the initial droplet radius is comparable to this thickness).

Subsequent evolution is affected by the presence

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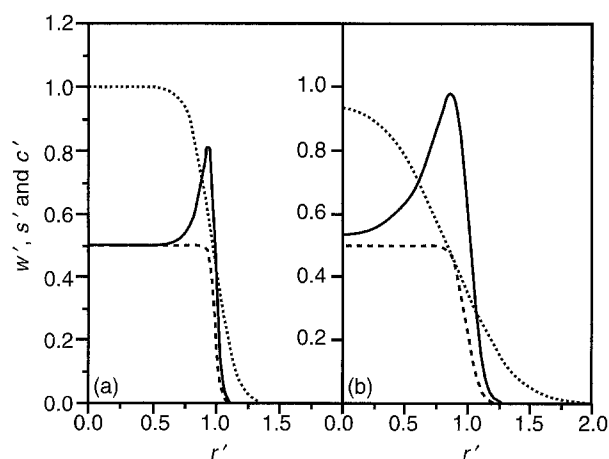


Figure 1 Profiles of (· · · · ·) dimensionless water (w') and (- - -) sol (s') concentrations, and (—) sol to water ratio (c') at (a) 10 and (b) 70 ms after the start of extraction.

of the membrane, which inhibits diffusion through it. Rather than complicate the model unduly, it will simply be assumed that all of the sol caught within the membrane eventually gathers on its inner surface, in a critical concentration with respect to water, and with all the alcohol excluded from the gel. The same approach is used for sol residing outside the membrane at the time of its formation. That is to say:

$$\int_0^{r_{\text{gel}}} 4\pi r^2 s(r, t = t_{\text{gel}}) dr = \frac{4\pi}{3} (r_{\text{gel}}^3 - r_{\text{inner}}^3) s_{\text{gel}} \quad (3)$$

where s_{gel} is the sol concentration in the gelled state, and r_{inner} is the inner radius of the gelatinous shell. This can also be written:

$$\int_0^{r_{\text{gel}}} 4\pi r^2 s' dr = \frac{4\pi}{3} (r_{\text{gel}}^3 - r_{\text{inner}}^3) \frac{w_{\text{gel}}}{w_0} \quad (4)$$

and we can then make the assumption that the water concentration in the gel w_{gel} is approximately equal to w_0 . A similar treatment leads to a determination of the outer radius of the gelatinous shell, r_{outer} .

The aspect ratio of the microcapsule is defined as the outer radius r_{outer} divided by the shell thickness ($r_{\text{outer}} - r_{\text{inner}}$). A value greater than unity indicates a hollow particle. It is assumed that this characterization of the geometry is unaffected by the drying and calcination stages by which the gelatinous microcapsule is transformed into a hollow ceramic powder particle.

The dependence of the aspect ratio of the ceramic particles on the initial concentration of the sol was studied in [1] and the findings are shown in Fig. 2. Alumina, silica and mullite powders were produced. Also shown are calculations made with the model described in [1] illustrating the good agreement for concentrated sols, but the failure to account for the behaviour at low initial sol concentrations. Model predictions from this work are also shown, for a number of choices of the ratio D_s/D_w . This is the only free parameter in the problem. Altering the droplet radius affects the time required for gelation, but not the geometry, as long as the initial radius is sufficiently greater than the critical shell thickness

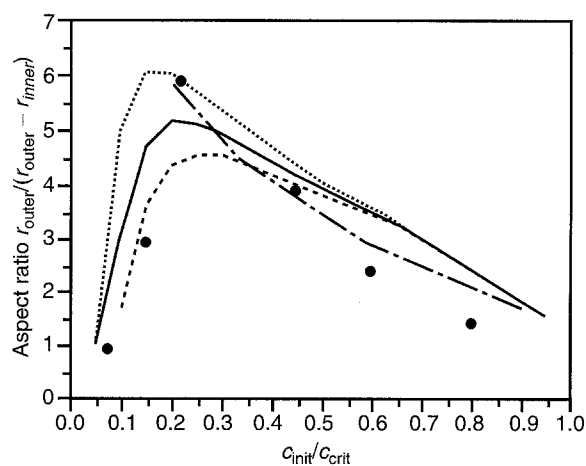


Figure 2 Particle aspect ratio against initial sol-to-water concentration ratio: comparison of model predictions with experimental results. $D_s/D_w =$ (· · · · ·), 0.03; (—), 0.04; (- - -), 0.05. (●), Experiment; (- - -), previous model.

required for rigid membrane formation. This is borne out by the observation in [1] that the smaller particles produced were usually solid and not hollow.

Each set of predictions from the present model can explain the occurrence of dense particles at the extremes of sol concentration. Although the sol diffuses much more slowly than the water, for very dilute initial sol concentrations, the sol to water ratio c first exceeds the critical value at the centre of the droplet, and hence a solid particle forms. A D_s/D_w ratio of 0.04 seems to provide the best fit to the data. For each value of D_s/D_w there is a maximum value of aspect ratio. This might be increased by reducing D_s , i.e. by suppressing sol diffusion, assuming the critical ratio c_{crit} remains the same for the modified sol.

In conclusion, a simple model of the diffusion of water and sol particles out of an aqueous droplet in a water-extracting environment has provided a rationalization of the observed dependence of particle geometry on initial sol concentration. A reasonable objection might be that the model is too simple, particularly in making the assumption that diffusion coefficients are constants for the two species in what is, in fact, a complex interacting system. Also, the development of the gel once the initial gelation criterion has been satisfied has been glossed over. However, the success of the model suggests that these simplifications are not untenable. Additional predictions by which the model might be tested are that the aspect ratio, the ratio of particle outer radius to shell thickness, is independent of the droplet initial radius (as long as the radius is greater than a minimum value), and that thinner shells might be produced by attempting to suppress the diffusion of the sol particles, by increasing their size, for example. It remains to be seen whether these suggested tendencies might be borne out in practice.

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