

Cavitation in Drying Droplets of Soft Matter Solutions

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When a droplet of a soft matter solution is dried, cavities are often formed in the droplet, giving a hollow sphere in the end. A theoretical model is given for this phenomenon. It is shown that the formation of a gel-like layer (skin layer), which has a finite shear modulus, is essential for the phenomenon to take place. The condition for cavity formation (how it depends on the shear modulus and thickness of the skin layer), and the variation of the droplet volume and cavity volume after the cavity formation are examined.

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When soft matter solutions (polymer solutions and colloidal suspensions) are dried, cavities are often formed in the dried material. The phenomena are frequently observed in spray drying [1,2]: a quick drying of small droplets of soft matter solutions in air. It is known that this process often produces hollow particles at the end of the process. The phenomena are important in many industries (materials, food, and pharmaceuticals), and also in the development of new functional particles [3–5]. Despite the importance, existing studies of the phenomena were done mostly from the application side, and not many studies have been done from the physics point of view. Accordingly, basic questions such as why and when cavities are formed have not been answered clearly. In this Letter, we shall give a simple theoretical model for the phenomena.

It is generally believed that cavitation is closely connected to the formation of a skin layer created at the surface of droplets during drying. The skin layer is a concentrated region of polymer or colloidal particles, and has a rheological property distinctively different from that of bulk solutions [6–8]. Recent experiments done for the slow drying of sessile droplets confirmed that cavities are formed after the skin layer is formed [9,10], but the precise relation between the skin layer and the cavity formation has not been clarified theoretically. Though it has been known that skin layers cause various instabilities in the drying droplet, such as the formation of dimples or wrinkles [11–14], the effect on the cavitation has started to be studied only recently [9,10].

To clarify the connection between the skin layer and the cavity formation, we consider a simplified problem, i.e., the drying of a spherical shell of a gel containing an inner solvent fluid [see Fig. 1(I)]. Here the gel is a model of the skin layer, and the inner solvent fluid is a model of bulk solutions. Clearly such a model neglects some important aspects of real systems: in reality, the skin layer is evolving: its mass and physical properties are changing in time, and

the inner fluid contains a solute whose spatial distribution is varying in time. Here we ignore these effects, and use a simple model to keep the analysis at a reasonably transparent level and to elucidate the essential physics in the mechanism of cavity formation. With this simple model, we can discuss why cavities are formed, and how the elasticity of the skin layer (the shear modulus and thickness) affects the cavity formation, etc.

Figure 1 is a sketch of the time evolution of our system. First a skin layer is formed at the surface of a droplet of a soft matter solution [Fig. 1(I)]. We regard the skin as a spherical shell of a gel, and consider the time evolution of the system after the gel is formed. The evaporation of the solvent is expressed by the weight loss of the droplet $\Delta W = W_0 - W$, where W_0 and W are the initial and the current mass of the droplet. With further evaporation of solvent, the droplet shrinks as in Fig. 1(II), and, under a certain condition, a cavity appears as in Fig. 1(III). If a cavity appears, the final state will be a hollow sphere as in Fig. 1(IV).

We shall discuss the time evolution of the system assuming that the droplet is in equilibrium for a given value of ΔW , and calculate the cavity size as a function of ΔW ; i.e., we shall discuss the evolution of the system as a function of ΔW , but not the time evolution of ΔW itself.

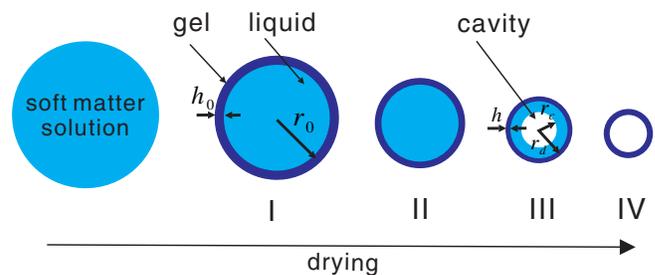


FIG. 1 (color online). Behaviors of a droplet of a soft matter solution in drying. See the text for explanation.

Now suppose that when a solvent of mass ΔW is taken out from the droplet, the droplet surface has a radius r_d , and that there is a cavity of radius r_c . We assume that both the solvent and solute are incompressible and have a constant density ρ . Then the mass conservation is written as

$$\Delta W = \frac{4\pi}{3}\rho[r_0^3 - r_d^3 + r_c^3], \quad (1)$$

where r_0 is the initial value of r_d .

We assume that the initial thickness of the gel, h_0 , is much smaller than r_0 . In such a case, each part of the gel shell is isotropically compressed in the plane tangent to the surface. Let λ_t and λ_n be the elongation ratios (current length/original length) in the plane and normal to the plane. They are given by

$$\lambda_t = \frac{r_d}{r_0}, \quad \lambda_n = \frac{h}{h_0}, \quad (2)$$

where h is the thickness of the gel in the current state. Equation (1) then gives

$$\lambda_t^3 = 1 - \frac{\Delta W}{W_0} + \left(\frac{r_c}{r_0}\right)^3. \quad (3)$$

The free energy of the system is written as

$$F_{\text{tot}}(\lambda_t, \lambda_n, r_c; \Delta W) = 4\pi r_0^2 h_0 f(\lambda_t, \lambda_n) + 4\pi r_c^2 \gamma + \frac{4\pi}{3} r_c^3 \Delta p, \quad (4)$$

where $f(\lambda_t, \lambda_n)$ is the free energy density of the deformed gel per unit volume (in reference to the initial state), γ is the surface tension, and Δp is the difference in the outer pressure p_{out} and the pressure in the cavity p_{in} , $\Delta p = p_{\text{out}} - p_{\text{in}}$.

Notice that Δp is positive in the usual condition since cavitation is not favored for the liquid. The value of p_{out} is clear, but the value of p_{in} needs some discussion. If the cavity is filled with solvent vapor, p_{in} is equal to the equilibrium bulk vapor pressure of the solvent. However, it has been shown that the cavity is usually filled with air (and other gas molecules dissolved in the solvent liquid) [15,16]. If air is dissolved in the solvent, p_{in} is equal to the pressure of the air when it is dissolved, and Δp is essentially zero. (In fact experimental measurement [9] indicates that Δp is small (less than 0.1 bar) and remains almost constant throughout drying.) From a theoretical viewpoint, p_{in} is a dynamical quantity, determined by the diffusion speed of the dissolved gas molecules [9]. In this Letter, we avoid such a complication, and proceed assuming that Δp is a positive constant.

In Eq. (4), we ignored the surface energy term of the gel phase (such as $4\pi\gamma r_d^2$ for the outer surface) since it is small

compared with the elastic energy. Though this is usually the case, corrections may be needed if the gel shell is very soft or very thin [17].

The explicit form of the deformation free energy $f(\lambda_t, \lambda_n)$ of a gel has been discussed in many literature sources (see, e.g., Refs. [18,19]). Using such expressions, we can calculate the equilibrium state by minimizing Eq. (4) for a given value of ΔW . This is done for two situations.

Small deformation.—If the deformation is small, $f(\lambda_t, \lambda_n)$ can be expressed by a quadratic form of the strain $\epsilon_t = \lambda_t - 1$ and $\epsilon_n = \lambda_n - 1$ as

$$f(\lambda_t, \lambda_n) = \frac{K_0}{2}(2\epsilon_t + \epsilon_n)^2 + \frac{2G_0}{3}(\epsilon_t - \epsilon_n)^2, \quad (5)$$

where K_0 and G_0 are the osmotic modulus and the shear modulus of the gel, respectively.

Notice that λ_t is constrained by ΔW and r_c [see Eq. (3)], but λ_n (or ϵ_n) can be determined independently of the other parameters. The condition $\partial f/\partial \lambda_n = 0$ gives $\epsilon_n = \epsilon_t[(4/3)G_0 - 2K_0]/[K_0 + (4/3)G_0]$, and Eq. (5) is written as

$$f(\lambda_t) = \frac{1}{2}K_e \epsilon_t^2 \quad \text{with} \quad K_e = \frac{12K_0G_0}{K_0 + (4/3)G_0}. \quad (6)$$

By Eq. (3), ϵ_t is expressed by the reduced cavity radius r_c/r_0 , or the reduced cavity volume $v_c = (r_c/r_0)^3$ as

$$\epsilon_t = \left[1 + \left(\frac{r_c}{r_0}\right)^3 - \frac{\Delta W}{W_0}\right]^{1/3} - 1 \approx \frac{1}{3}\left(v_c - \frac{\Delta W}{W_0}\right). \quad (7)$$

Hence the free energy is written as

$$F_{\text{tot}}^{\text{linear}} = \frac{1}{2}V_{g0}K_e \left[\frac{1}{9}\left(v_c - \frac{\Delta W}{W_0}\right)^2 + \frac{\ell_e}{h_0}v_c^{2/3} + \frac{\Delta p}{3p_e}v_c\right], \quad (8)$$

where $V_{g0} = 4\pi r_0^2 h_0$ is the initial volume of the gel shell, ℓ_e is the elastic length defined by $\ell_e = 2\gamma/K_e$, and p_e is defined by $p_e = K_e(h_0/2r_0)$.

Equation (8) is plotted as a function of v_c in Fig. 2. If ΔW is small, the free energy has a minimum at $v_c = 0$, so there is no cavity. When ΔW becomes large, the free energy curve starts to have another local minimum at a positive value of v_c . The critical point at which such a local minimum appears is determined by $\partial F_{\text{tot}}/\partial v_c = \partial^2 F_{\text{tot}}/\partial v_c^2 = 0$. This gives the following critical cavity volume v_c^* and weight loss ΔW^* :

$$v_c^* = \left(\frac{\ell_e}{h_0}\right)^{3/4}, \quad \frac{\Delta W^*}{W_0} = 4\left(\frac{\ell_e}{h_0}\right)^{3/4} + \frac{3\Delta p}{2p_e}. \quad (9)$$

With further increase of ΔW , the value of the local minimum decreases and becomes equal to that at

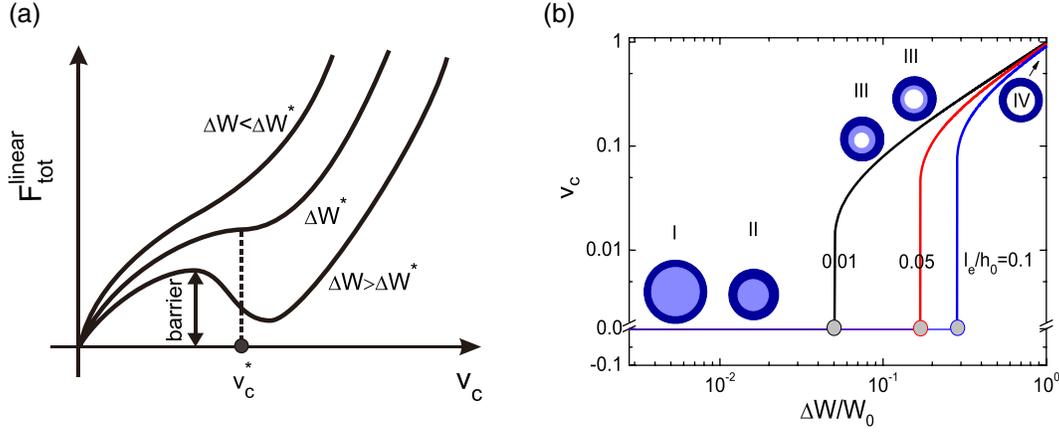


FIG. 2 (color online). (a) Free energy of the system plotted as a function of reduced cavity volume $v_c = (r_c/r_0)^3$ for various weight losses ΔW . (b) Reduced cavity volume $v_c = V_c/V_0$ plotted as a function of reduced weight loss $\Delta W/W_0$.

$v_c = 0$. The weight loss $\Delta W^{(e)}$ at this state is of the same order of ΔW^* , i.e., $\Delta W^{(e)} = 2(3\ell_e/h_0)^{3/4} + 3\Delta p/2p_e$. If the system can choose to take a state of minimum free energy, a cavity will appear when ΔW becomes equal to $\Delta W^{(e)}$. However, it is known [15,20,21] that such a thermodynamic argument usually does not work since the cavitation of gas molecules dissolved in liquids is strongly affected by nanosized bubbles or contaminant particles. In this Letter, we shall avoid this issue, and proceed regarding ΔW^* as the characteristic weight loss at which cavities appear.

The theory described above gives the following physical mechanism for cavitation. As the solvent evaporates, the gel is compressed, and the elastic energy of deformation increases. To reduce the elastic energy, a cavity is created. Notice that in this mechanism, it is essential for the skin phase to have a finite shear modulus. If the shear modulus G_0 is zero, K_e is equal to zero, and cavities never appear during the drying process.

The critical weight loss ΔW^* decreases with the increase of the elastic constant K_e and the gel thickness h_0 , i.e., with the increase of the compression modulus of the gel slab. This is natural since the driving force for the cavity formation is the elastic force of the compressed gel shell.

Large deformation.—Though the linear theory is convenient to understand the physics in a simple form, it is not accurate in practice since the actual value of the critical strain $\epsilon_t^* = (1/3)(v_c^* - \Delta W^*/W_0)$ is large. In such a case, a nonlinear theory is needed. Here we show a result of such a nonlinear analysis using the following expression for the elastic deformation of polymeric gels [18,19]

$$f(\lambda_t, \lambda_n) = \frac{G_0}{2} \left[2\lambda_t^2 + \lambda_n^2 - 3 + \frac{1}{n_0 v_m} \frac{\phi_0}{\phi} [(1-\phi) \ln(1-\phi) + \chi\phi(1-\phi)] \right], \quad (10)$$

where G_0 is the shear modulus, ϕ_0 is the volume fraction of polymer in the gel at its initial state, $\phi = \phi_0/(\lambda_t^2 \lambda_n)$ is the volume fraction at the current state, n_0 is the number of subchains per unit volume, v_m is the molecular volume of a polymer segment, and χ is the Flory-Huggins parameter representing the affinity between the polymer and the solvent.

By Eqs. (4) and (10), the free energy of the system can be expressed as a function of v_c . The equilibrium value of v_c is determined by minimizing the free energy for values of ΔW . A result of such a calculation is shown in Fig. 3, where the reduced cavity volume $v_c = (r_c/r_0)^3$ and the reduced droplet volume $v_d = (r_d/r_0)^3$ are shown as a function of ΔW by solid lines. For comparison the corresponding curve obtained by the linear theory is shown by dashed lines [18]. Both the linear and nonlinear theories predict that a cavity appears when ΔW exceeds a critical value ΔW^* , but the

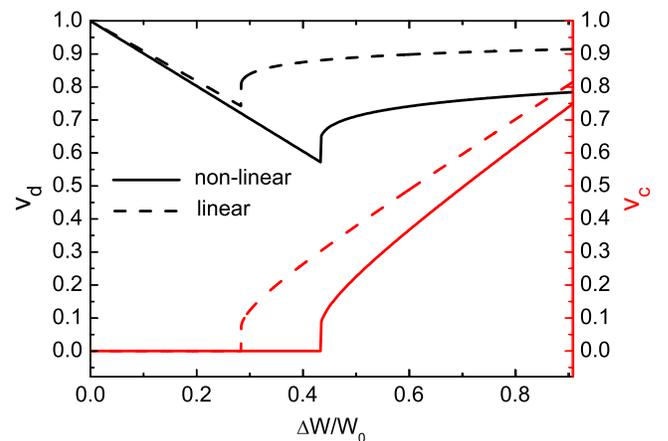


FIG. 3 (color online). Reduced apparent volume of the droplet, $v_d = V_d/V_0 = (r_d/r_0)^3$, and that of the cavity, $v_c = V_c/V_0 = (r_c/r_0)^3$, plotted against the reduced weight loss of the droplet $\Delta W/W_0$. The curves are obtained with the use of Eq. (10) for $\ell_e/h_0 = 0.1$, $\Delta p/p_e = 0$, $n_0 v_m = 10^{-2}$, and $\chi = -0.1$.

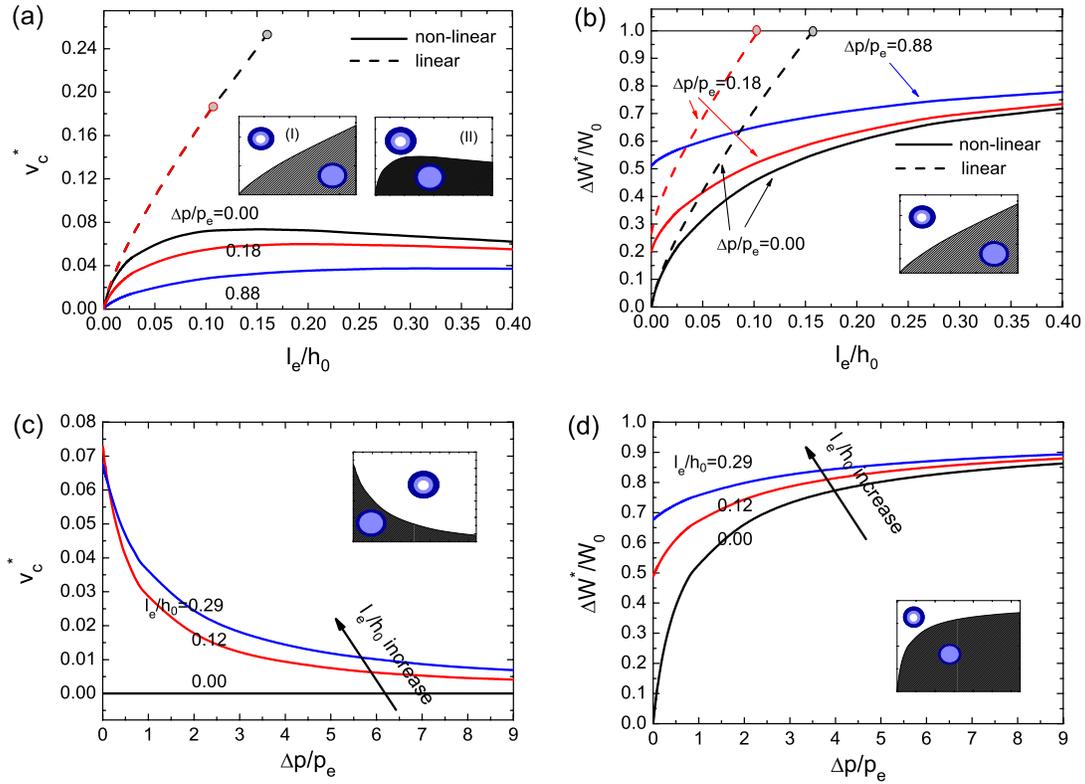


FIG. 4 (color online). (a) Critical cavity volume v_c^* plotted as a function of ℓ_e/h_0 for various values of $\Delta p/p_e$. Results of the linear theory are shown by the dashed lines. (b) Critical weight loss ΔW^* plotted as a function of ℓ_e/h_0 . (c) Critical cavity volume v_c^* plotted as a function of $\Delta p/p_e$. (d) Critical weight loss ΔW^* plotted as a function of $\Delta p/p_e$. Parameters used in the nonlinear calculations are $\chi = -0.1$ and $n_0 v_m = 10^{-2}$.

value of ΔW^* is different for the two theories, which indicates the necessity of the nonlinear analysis.

Notice that once a cavity is created, the droplet volume v_d stops decreasing, or even increases slightly with the increase of ΔW : once a droplet is created, the evacuated volume of solvent is filled by the cavity, and the apparent volume of the droplet does not change significantly. Therefore the apparent size of the dried droplet is essentially determined by the critical volume at which the stable cavity is created.

Figures 4(a) and 4(b) show how v_c^* and $\Delta W^*/W_0$ depend on ℓ_e/h_0 . [Here the result is shown in the range of $\ell_e/h_0 < 0.4$ since for large values of ℓ_e/h_0 , Eq. (4) becomes incorrect as the surface tension of the gel phase becomes non-negligible.]

When ℓ_e/h_0 is small, the deformation is small at the critical point. In this case the result agrees with that of the linear theory; i.e., both v_c^* and ΔW^* increase with the increase of ℓ_e/h_0 . On the other hand, the nonlinear analysis gives a prediction qualitatively different from that of the linear analysis. As shown in Fig. 4(a), the critical cavity volume v_c^* has a maximum as a function of ℓ_e/h_0 , and decreases with the increase of ℓ_e/h_0 for large ℓ_e/h_0 .

The behavior for large ℓ_e/h_0 can be understood as follows. For a large deformation, the elastic energy

becomes less sensitive to strain due to the nonlinear elasticity of the polymer network. Therefore, the horizontal axis $\ell_e/h_0 = 2\gamma/(K_e h_0)$ can be viewed as a change of the surface tension γ . With the increase of surface tension, smaller cavities are favored, and therefore v_c^* decreases.

Figures 4(c) and 4(d) show how v_c^* and ΔW^* depend on Δp . With the increase of Δp , the cost of creating a cavity increases [see Eq. (4)], and therefore ΔW^* increases. On the other hand, v_c^* decreases since again smaller cavities are favored for large Δp .

We now discuss the relevance of the theory to experiments. Sadek *et al.* [10] reported that in the drying of whey protein solutions, a cavity appears when the droplet weight decreases by 40% of the initial weight. On the other hand, our theory gives $\Delta W^*/W_0 = 0.4$ if we estimate the physical parameters from their paper ($h_0 = 20 \mu\text{m}$, $G_0 = 10 \text{kPa}$, $\gamma = 80 \text{mN/m}$). This indicates that our theory is giving the right order of magnitude for the cavitation condition. Furthermore, their observation that the apparent volume of the droplet V_d remains almost constant after the cavity is formed is consistent with our theoretical result shown in Fig. 3.

The system studied here is an idealization of real systems. In reality, the actual problem is much more complicated. The skin layer is probably a viscoelastic

liquid, and its thickness and relaxation time vary as drying proceeds. Moreover, the pressure difference may change during the whole process. However, we believe the mechanism underlying these phenomena has been given here. We will report the result of more realistic models in a separate paper.

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