ME 574 Final Course Project

The Evaporation and Rehydration Process of Aqueous Two Phase System (ATPS)

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Introduction

Evaporation of liquids on substrates is an important effect in many microscale applications, such as lab-on-a chip systems. When the liquids are in droplets, the large surface area to volume ratio makes the evaporation dominate the interface migration. In this project, we derive the theory and perform a numerical method to simulate the evaporation and rehydration process of an aqueous polymer two phase system (ATPS). ATPS is a common liquid separation process which is composed by two different polymer solutions, such as polyethylene glycol (PEG) and Dextran (DEX). Here, we first simulated the evaporation process of DEX solutions into the vapor environment. After that, we simulated the rehydration process by dropping PEG solutions onto the dried DEX surface. From our numerical model, we had successfully modeled the surface profile change and discussed how the substrate property and the humanity of environment would affect the final result.

Theory

There are two major parts in this project. The first is the natural evaporation of the droplet. The other is the rehydration process. Our system starts with a droplet of Dextran (DEX), see figure 1 below. Its initial size and contact angle are based on our experimental measurement. The free energy of the droplet can be modeled with

$$G = \int r dA + gV \qquad (1)$$

where the integration resembles the surface energy and the second term is the energy of the body volume.

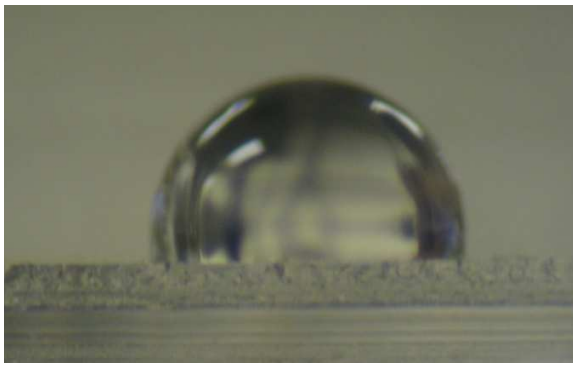

Fig. 1 – Dextran droplet from experiment.

The interface between the liquid and the vapor undergoes a virtual motion (figure 2). This motion results a small virtual migration,δr_n, which varies from point to point over the surface. Due to this virtual surface migration, the free energy of the system also varies by δG. This change can be represented by

$$\int P\delta r_n dA = -\delta G \qquad (2)$$

where P is the thermodynamic force.

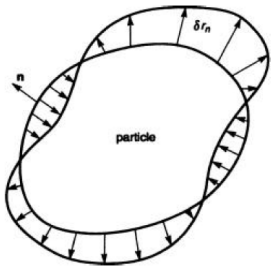

Fig. 2 – Virtual migration on the interface between the liquid and the vapor.

In equation 2 above, we can replace the driving pressure with the interface velocity, v_n, which is equal to the product of driving pressure and material mobility. The resulting expression becomes

$$\int \frac{v_n}{L} \delta r_n \, dA = -\delta G \qquad (3)$$

When the surface tension is isotropic, the liquid-vapor interface at a given time is usually a smooth surface and the free energy can be represented with equation 1. The surface velocity? is governed by

$$v_n = -L(\gamma K + g) \qquad (4)$$

where L and γ are mobility and surface tension, respectively. K is the sum of the principal curvatures.

Combining equation 3 and 4, one can reached the following conclusion,

$$\int L(\gamma K + g)\, \delta r_n \, dA = \delta G \qquad (5)$$

As one can observed from the above equation, there are several material parameters that must be determined either through literature researches or experiments. These parameters include mobility, surface, and volume energy density. We were only able to find a value for DEX surface energy density. Its mobility will be normalized and we will determine its volume energy density by fitting the simulation result into experimental results

The evaporation process is expected to happen until an equilibrium state occurred. Figure 3 below illustrates the Dextran droplet after evaporation. When this state has been reached, a drop of polyethylene glycol (PEG) is added to the system and rehydration will start (figure 4). In terms of the free energy equation, the only different between evaporation and rehydration is the volume energy density, Δg. In the prior case, Δg is the difference between DEX and ambient air. In the latter case, it is the difference between DEX and PEG.

Fig. 3 – Dextran droplet after evaporation.

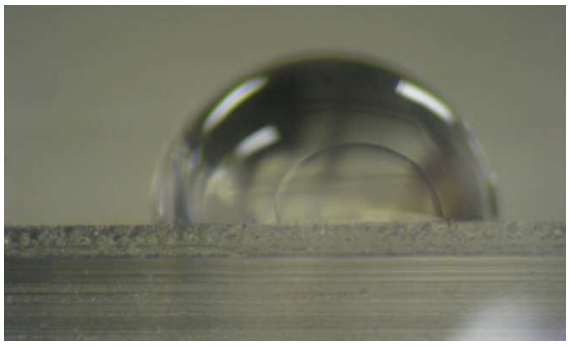

Fig. 4 – Added PEG solution to rehydrate Dextran droplet

Numerical methods

The phenomena mentioned in the previous section are simulated using the finite element analysis (or FEA) approach. To simplify the structure, we took a cross-sectional cut at the droplet and apply FEA to this two-dimensional structure. Figure 5 shows our two-dimensional model in MATLAB.

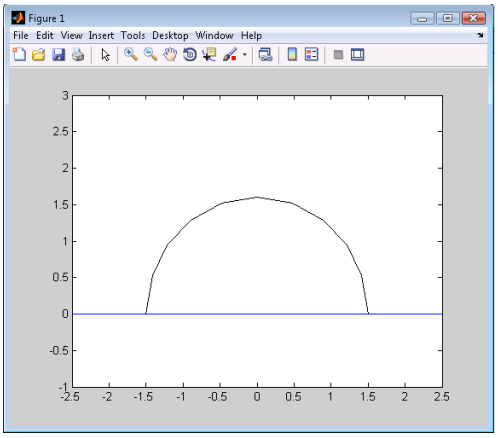

Fig. 5 – Two-dimensional model of droplet cross section.

The droplet surface can be modeled with many discrete straight line elements. Each element consists of two nodes and a line. Figure 6 below illustrates a simple element.

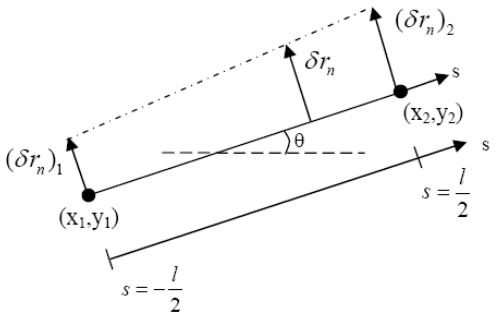

Fig. 6 – A straight line element, two nodes and one line.

From the figure, we can express the virtual migration as the following

$$\delta r_n = N_1 \delta x_1 + N_2 \delta x_1 + N_3 \delta x_2 + N_4 \delta y_2 \qquad (6)$$

where N_i's are the interpolation coefficients and can be represented by

$$N_1 = -\left(\frac{1}{2} - \frac{s}{l}\right) sin\ \theta, N_2 = \left(\frac{1}{2} - \frac{s}{l}\right) cos\ \theta, N_3 = -\left(\frac{1}{2} + \frac{s}{l}\right) sin\ \theta, N_4 = \left(\frac{1}{2} + \frac{s}{l}\right) cos\ \theta \qquad (7)$$

Similarly, the interface velocity relates to the nodal velocities, $\dot{x}_1, \dot{y}_1, \dot{x}_2, \dot{y}_2$ by

$$v_n = N_1 \dot{x}_1 + N_2 \dot{y}_1 + N_3 \dot{x}_2 + N_4 \dot{y}_2 \qquad (8)$$

There are two main groups of nodes involved, the middle and the end nodes. The middle nodes only involve surface tension force, while the end nodes have additional frictional force due to the substrate. The surface tension depends on the crystalline orientation of the interface, resembled by $\gamma(\theta)$. For our two-dimensional structure, the total free energy is

$$G = \int \gamma(\theta)\, dA + \sum gV \qquad (9)$$

The first term is over the lengths of all the elements, and the second term is over areas of all the phases.

When one examine the virtual motion of a single element, equation 9 can be rewritten as

$$\delta G = \gamma \delta l + \frac{d\gamma}{d\theta} l \delta\theta - (g^I - g^{II}) l \frac{(\delta r_n)_1 + (\delta r_n)_2}{2} \qquad (10)$$

The first part deals with the elongation of the element; the second due to the rotation; and the third due to the trapezoidal area swept by the motion, where the two 'g' are the free energy densities of the two bulk phases. We can express the free energy variation in terms of virtual motions of the nodes

$$\delta G = -f_1 \delta x_1 - f_2 \delta y_1 - f_3 \delta x_2 - f_4 \delta y_2 \qquad (11)$$

where f_i, the forces acting on the nodes, can be expressed as

$$\begin{Bmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \end{Bmatrix} = \gamma \begin{Bmatrix} \cos\theta \\ \sin\theta \\ -\cos\theta \\ -\sin\theta \end{Bmatrix} + \frac{d\gamma}{d\theta} \begin{Bmatrix} -\sin\theta \\ \cos\theta \\ \sin\theta \\ -\cos\theta \end{Bmatrix} + l \frac{(g^I + g^{II})}{2} + f_r(f_i) \qquad (12)$$

The last term is slightly modified to factor in the frictional force (viscous force). This term would only exist in the nodes facing to the surface, not in the middle nodes. Its magnitude should not be greater than the projected horizontal force f1. For the leftmost node, it can be expressed as the following

$$if\ |f_{ro}| \geq f_1, then\ f_r = f_1, else\ f_1 = f_{ro} \qquad (13)$$

Combining the previous equation 3 with equation 11 and 12, we can rewrite it as

$$\int \frac{v_n}{L} \delta r_n\, dA = \{\delta x_1 \quad \delta y_1 \quad \delta x_2 \quad \delta y_2\} \left[H_{ij}\right] \begin{Bmatrix} \dot{x_1} \\ \dot{y_1} \\ \dot{x_2} \\ \dot{y_2} \end{Bmatrix} \qquad (13)$$

where $\left[H_{ij}\right]$ is a 4 x 4 symmetric matrix calculated from

$$\left[H_{ij}\right] = \frac{1}{L} \int_{-l/2}^{l/2} N_i\, N_j\, ds \qquad (14)$$

Finally, the weak statement can be written as

$$(\delta x)^T H\dot{x} = (\delta x)^T f \quad or \quad H\dot{x} = f \qquad (15)$$

Equation 15 is the differential equation that must be solved; however, instead of solving it analytically, we will solve it using Euler's Method (equation 16) in MATLAB.

$$y_{n+1} = y_n + hf(y_n) \qquad (16)$$

Results

Evaporation

In the case of an ideal fluid or inviscid fluid which has no resistance to shear stress, the droplet should keep the spherical shape during evaporation process. Fig.7 shows the evaporation process of an ideal fluid.

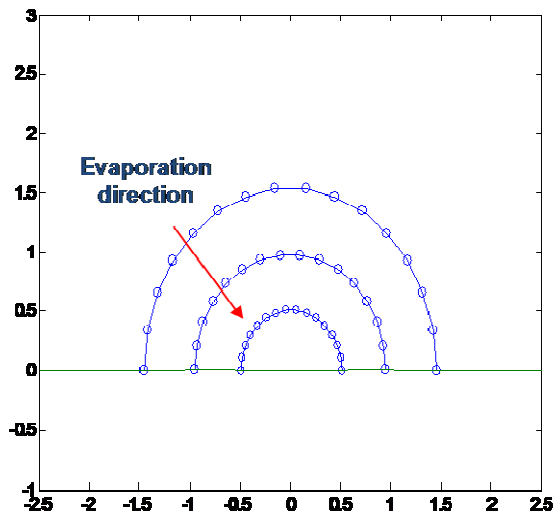

Fig. 7 – Evaporation process without frictional forces (ideal fluid)

As shown in the Fig.7, The nodes of the droplet with no friction (ideal fluid), which are corresponding to surface molecules, have shrunk at the same rate. In all real fluids except superfluids, however, there exists some resistance which is being deformed by either shear stress or extensional stress. The frictional forces between DEX and substrates make the molecules of DEX nearby the substrate clung to the surface of substrates, thereby causing some molecule-depletion region (Fig. 8) in the middle of the crest and the bottom of the droplet. In other words, surface

molecules tend to move either to the substrate due to the viscosity or to the crest of the droplet by surface tension during evaporation process. Thus, the frictional forces of fluid were applied to our simulation. The result is shown in Fig. 9.

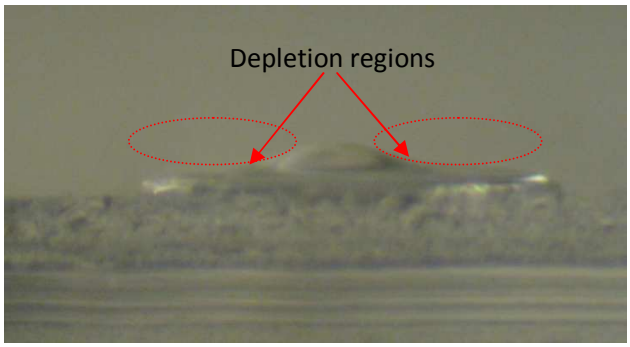

Fig. 8 – Viscosity effect on evaporation

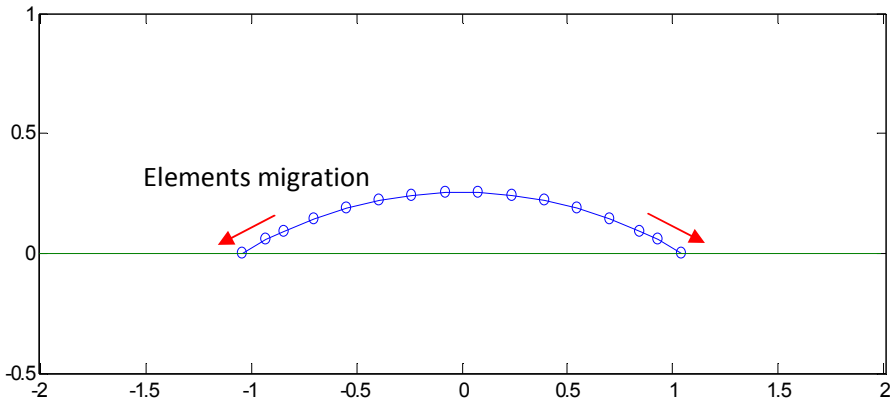

Fig. 9 – Droplet shape after evaporation

In this simulation, surface tension is assumed to be 2.4 while the free energy densities, g1 and g2, are set to 0.9 and 0.2, respectively. Fig.9 shows that the nodes close to the surface of the substrate were condensed near the substrate and the middle nodes of the droplet including the crest were located and shrunk uniformly, as expected. Therefore, we have observed that the simulation result is in good agreement with the experimental evaporation data.

Rehydration

Rapid recovery of the contact angle which is corresponding to filling up depletion of molecules of the droplet after evaporation is expected in the rehydration process due to the large difference of the volume energy density, Δg, between DEX (low volume energy density caused by molecule depletion) and PEG (high volume energy density). Fig. 10 shows how fast the contact angle is recovered when the rehydration starts. The contact angle increased drastically as soon as PEG was added as one would expect.

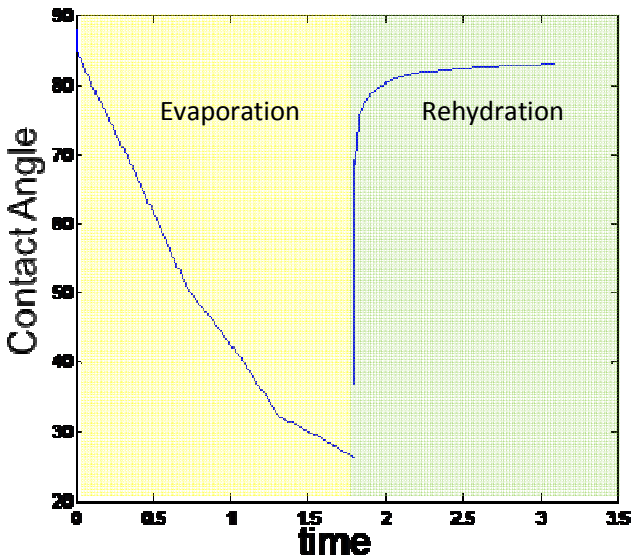

Fig. 10 – Contact angle changes during evaporation and rehydration processes

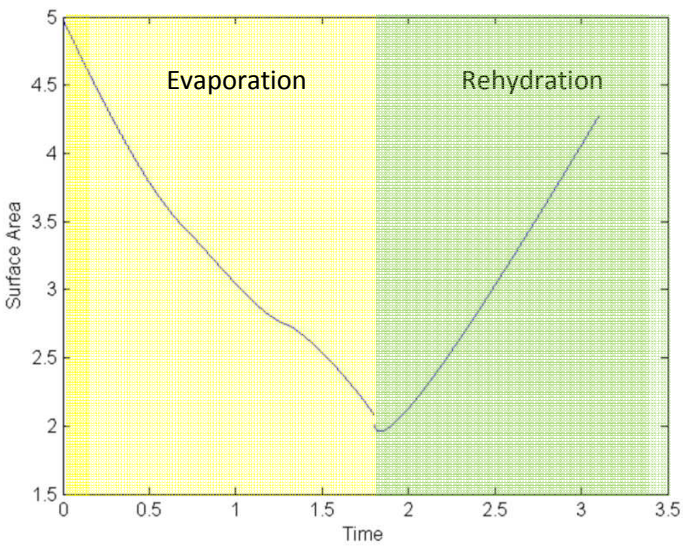

Fig. 11 – surface area changes during simulated evaporation and rehydration processes

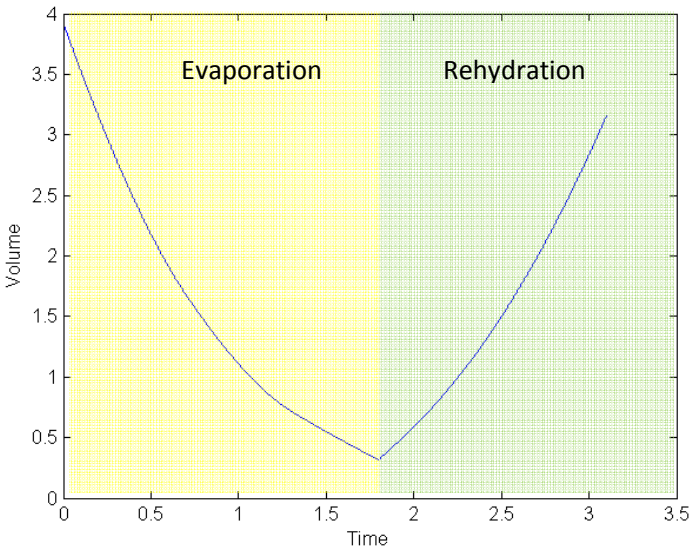

Fig. 12 – Volume changes during simulated evaporation and rehydration processes

Above figures show the evolution of the surface area and volume over the elapsed time. From Fig. 11, we can observe that the surface area increases at a steady rate in the rehydration process. The possible reason is that the contact angle rapidly increases to around 90 degree, which create an uniform surface profile is the beginning. We can also find out the similar situation in the volume evolution process, as shown in Fig. 12.

From the above simulated evaporation and rehydration process, we can compare them with experimental results. As shown in video files, they both show excellent agreement in the surface profile alteration. The contact angle shrink rate decreased in the end because of viscous fluid. In the rehydration process, the contact angle growing rate is shaper than shrink rate. It rapidly recovered to almost 90 degree in small time period. Both experimental and simulation results showed this phenomenon.

Conclusions

In this project, we successfully use the finite element analysis to simulate the evaporation and rehydration process of an aqueous polymer two phase system. In the real situation, it is a complicate dynamic process. We cannot easily calculate the droplet volume or contact angle over the elapsed time, which is important for sample concentration calculation in the biomedical application. By this simulation method, the evolution of contact angle, surface area and volume can be calculated and be compared with the experimental results. Once we find out the correlation between the simulated and experimental parameters, we can simply change simulation parameters to evaluate the effect of substrate roughness, environmental temperature and humidity in the evaporation and rehydration process. It can help us to modify these parameters and improve the experimental result.

References

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