

# Soft Matter

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# Comment on “An alternative theory to explain the effects of coalescing oil drops on mouthfeel” by B. Le Reverend and J. Engmann, *Soft Matter*, 2015, **11**, 7077

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The article “An alternative theory to explain the effects of coalescing oil drops on mouthfeel” provided a physical scenario that involves two phases in parallel and claimed that phase separated state of emulsion is more viscous than homogeneous emulsion before phase separation. However, two questions are raised.

First, although the authors claimed that they want to address the difference between predictions by tribometers and human perception, the viscosity change in their physical image should be able to be detected by tribometers, since the increase of viscosity predicted in their model will cause the increase of friction. Second, when they derive the equations, they use  $\eta_e$  to denote the viscosity of emulsions both before and after phase separation. The relation between viscosity of emulsion and droplet fraction follows approximately linear rule  $\eta/\eta_s=1+2.5\phi$ , and the volume fraction of droplet in emulsion decrease when phase separation happens. This will cause the total viscosity to decrease as well. We tried to reconstruct their model to incorporate the effect of decreased viscosity of emulsion due to lower oil volume fraction. In figure.1, left side is emulsion before phase separation. It has oil volume fraction  $\phi_0$ . After phase separation, on the right side of figure.1, the upper separated oil occupies  $\phi_c$  of the total volume fraction, where c denotes “cream”. We derived a new equation (see justification material):

$$r \equiv \frac{\sigma'}{\sigma} = \frac{1}{\alpha(1+2.5\phi_0)} \quad (1)$$

$$\alpha \equiv \frac{\phi_c}{s} + \frac{(1-\phi_c)^2}{1-3.5\phi_c+2.5\phi_0} \quad (2)$$

$$s \equiv \frac{\eta_{oil}}{\eta_s} \quad (3)$$

r larger than 1 means the viscosity increase due to phase separation, and *vice versa*. When  $\phi_c=0$ , r is equal to 1. Notice that there are only 3 free parameters: s,  $\phi_0$  and  $\phi_c$ . So we plot r against either s or  $\phi_c$  at different parameter conditions. In fig.2(A), we set  $s=1000$ , which is a rather high value for emulsion, and plot r against  $\phi_c$  for different  $\phi_0$ . At low  $\phi_0$ , r keeps decreasing with increase of phase separation progress. When  $\phi_0$  increases, r started to show a maximum, which reflects the tradeoff between the effect of oil layer and effect of diluter emulsion. However, we notice that when the emulsion is totally phase separated, the final viscosity is smaller than initial viscosity, even for very high s ratio. In fig.2(B),

we set  $\phi_0=0.5$  and plot  $r$  against  $\phi_c$  for different  $s$ . We can see that  $r$  varies significantly at low  $s$  but only change slightly at high  $s$ . This is further illustrated in figure1(C), where we keep  $\phi_c=0.1$  and plot  $r$  against  $s$ . In figure.2(C), we can see that with same amount of creamed oil, higher initial oil content consistently lead to higher  $r$ . We also can see from this figure the effect of  $\phi_c$  to be hard to interpret although it can be better understood in figure.2(B). This could be one reason for the mouthfeel to be difficult to predict. All curves showed plateau at high  $s$ , which is expected since the compliance of lower emulsion phase dominates when  $s$  is high. Finally, in figure.2(D), we set  $\phi_0=0.5$ , and plot  $r$  against  $s$ . We can see an inconsistent pattern with  $\phi_c$  at intermediate and high  $s$  which can be explained by figure.2(B). However, we see at low  $s$  that phase separation lead to monotone decrease of  $r$ , which is also expected because the viscosity gain due to oil layer cannot compensate the loss of viscosity due to lower emulsion concentration at low  $s$ .

### Further considerations

We need to further address that this model is still simplified by ignoring the effect of hydration layer around emulsion droplet, and redistribution of emulsifier. Further development of model is need especially for the latter one since the first one consistently lead to lower  $r$  because droplet size will increase in parallel with phase separation.

Another refinement involves better prediction of viscosity at high volume fraction of droplet. We adopt the equation suggested by Carlos et al.[1]. The relation between relative viscosity and volume fraction is

$$\eta_r \left( \frac{2\eta_r + 5S}{2+5S} \right)^{\frac{3}{2}} = \left( 1 - \frac{\phi}{\phi^*} \right)^{-\frac{5}{2}} \quad (4)$$

$$\eta_r \equiv \frac{\eta}{\eta_s} \quad (5)$$

The value of close packing parameter  $\phi^*$  is set to 0.68[2]. Notice that in this equation the relative viscosity of two phases takes place [3]. We then plot  $r$  against  $\phi_c$  at different  $\phi_0$  and  $s=50$  (fig.3A). In this case  $r$  monotone decreases with  $\phi_c$ . This suggests that due to higher dependency of  $r$  on volume fraction, the same drop of volume fraction will induce larger drop of viscosity. We also plot  $r$  against  $\phi_c$  for different  $s$  (fig.3b). Surprisingly, except the smallest  $\phi_c$ ,  $r$  decrease with  $s$ . This suggests that modeling oil droplet as hard sphere in oil-in-water emulsion may be an oversimplification for application. We also want to briefly discuss the continuous formation of oil layer at tongue and upper jaw. With successive flow of emulsion through, more and more oil will deposit until a thickness that shear stress will cause significant flow of the layer. The net effect of thickening oil layer is equal to decrease bulk oil viscosity (although they are not the same) in the equation of  $r$ . So we expect the effect would be superposition to increase of  $s$ .

The slip between two liquid phases, however, can be neglected because the slip length (up to 20 times of molecular size) [4, 5] is many orders smaller than thickness of liquid layer we discussed here. We finally want to discuss the inclusion of water in separated oil phase. If happens, it will increase the viscosity of both oil phase (similar to the case of oil in water but with factor close to 1 rather than 2.5)[3], and water phase (due to concentrate of emulsion). The solubility of water in oil is below 1% at

ambient temperature without surfactant[6]. In case of phase separation of oil-in-water emulsion, this effect may also be small due to high HLB of surfactant used. However, in practice a combination of high and low HLB surfactants are usually used for better performance[2]. When phase separate the low HLB surfactant will partite more in oil phase thus facilitate water in oil emulsions. So the degree of water inclusion will depends on many factors of oil and surfactant. To briefly describe the effect we include  $S_w$  as the volume fraction of water in separated oil phase relative to the volume of separated oil. In fig.4 we plot  $r$  against  $\phi_c$  for different  $S_w$ . Clearly  $r$  increase with  $S_w$  as expected. But we still don't have any knowledge of the practical range of  $S_w$ .

Finally, although with above mentioned, one step ahead will make better explanation that is compatible with the first question raised in the start of comment. The phase separation will cause the water rich layer drain faster than the upper oil layer, thus the water layer will become thinner and left a thick oil layer. The time scale of leftover oil layer state is proportional to its viscosity. So the human perception of higher viscosity can be attributed to the oil layer from phase separation. The convection rate of lower emulsion is  $s$  times lower than the oil layer, which means, if  $s=50$ , which is close to values of typical vegetable oils, only  $1/50$  layer thickness of emulsion will remain compared to the oil layer. Meanwhile, oil layer will also contribute longer time in perception process than the whole emulsion with a ratio positively related to  $s$ . The model is depicted in fig.5. The water and oil phases become two parallelograms with fixed baseline length and height. The distance of deformation of each parallelogram is proportional to the initial volume fraction ratio over viscosity of that phase, i.e.  $\phi_i/\eta_i$ . The thickness of the layer could be considered as the average thickness of each phase that doesn't fall out from original rectangle.

In conclusion, by introducing decrease of emulsion viscosity, we improved the previously published model, and illustrated the effect of oil viscosity, initial oil content and extent of phase separation on viscosity of phase separated emulsion. Whether phase separation lead to increase or decrease of viscosity depends on the specific location of parameters. Noticeably, when  $\phi_0$  is high, the total viscosity first increase then decrease with phase separation progress. We also tentatively try to explain the difference between tribometer and human perception by introducing the effect of different convection rate of phase separated layers.

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4. Galliero, G., *Lennard-Jones fluid-fluid interfaces under shear*. Physical Review E, 2010. **81**(5): p. 056306.
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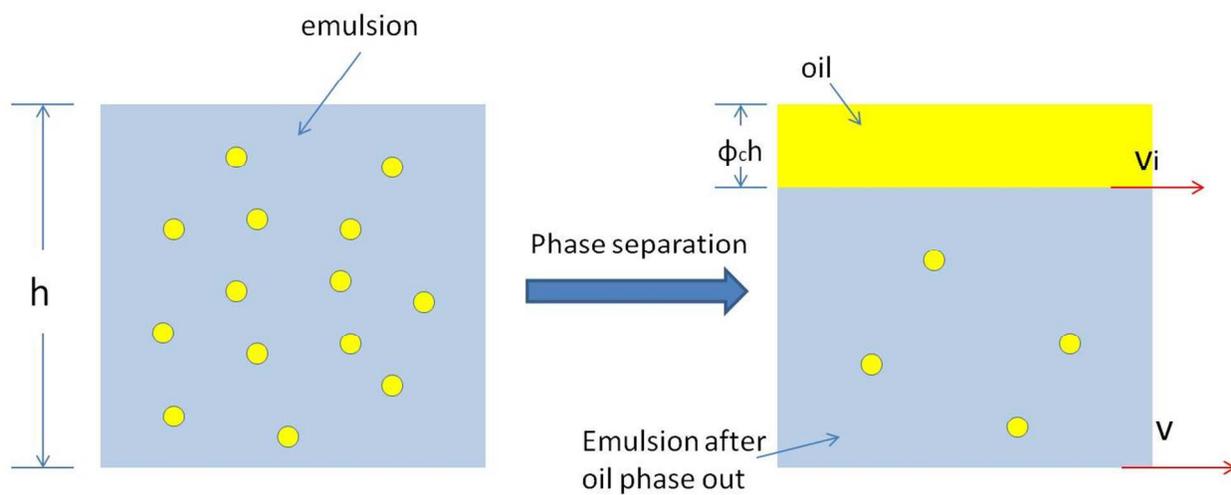


Figure.1 Schematic description of emulsion phase separation.

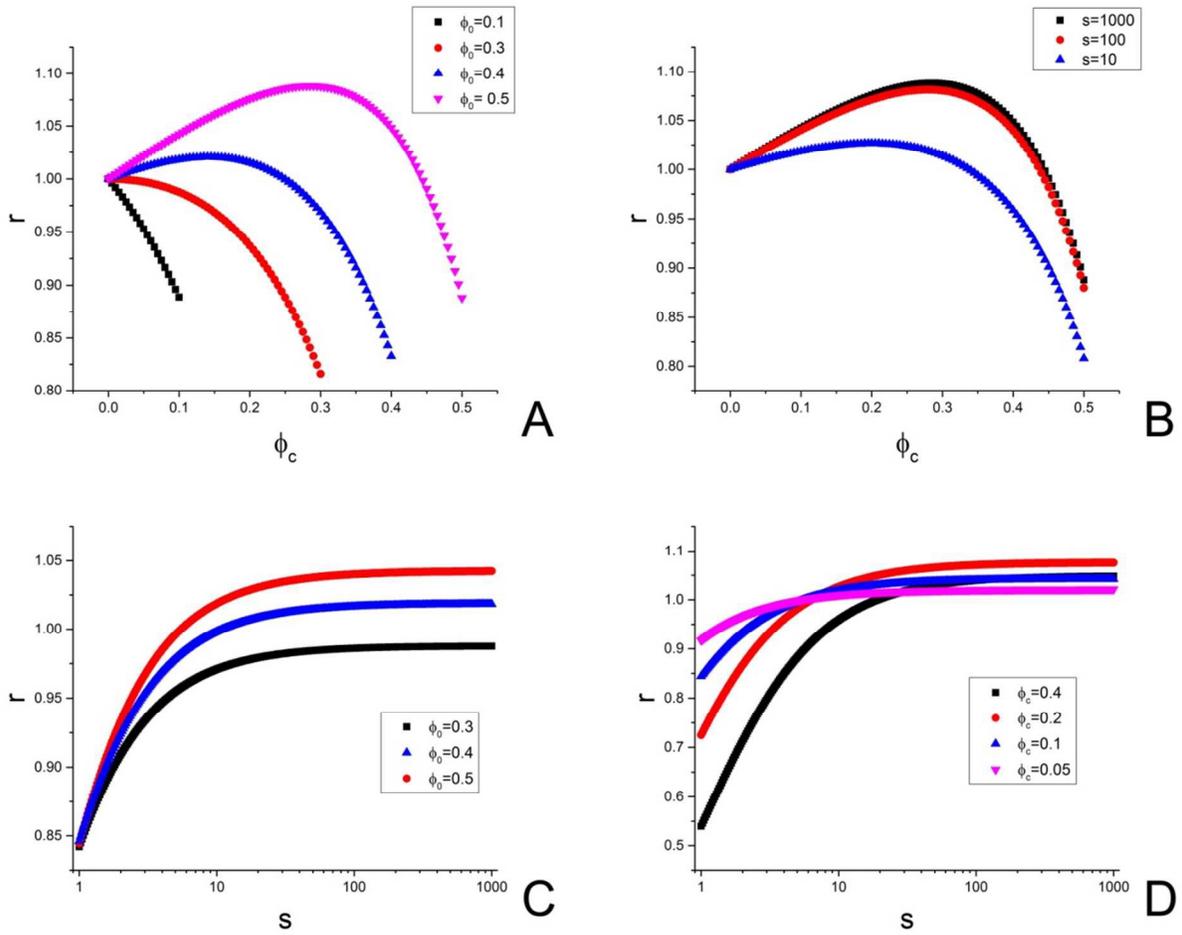


Figure.2. A: plot of  $r$  against  $\phi_c$ ,  $s=1000$ ; B: plot of  $r$  against  $\phi_c$ ,  $\phi_0=0.5$ ; C: plot of  $r$  against  $s$ ,  $\phi_c=0.1$ ; D: plot of  $r$  against  $s$ ,  $\phi_0=0.5$ .

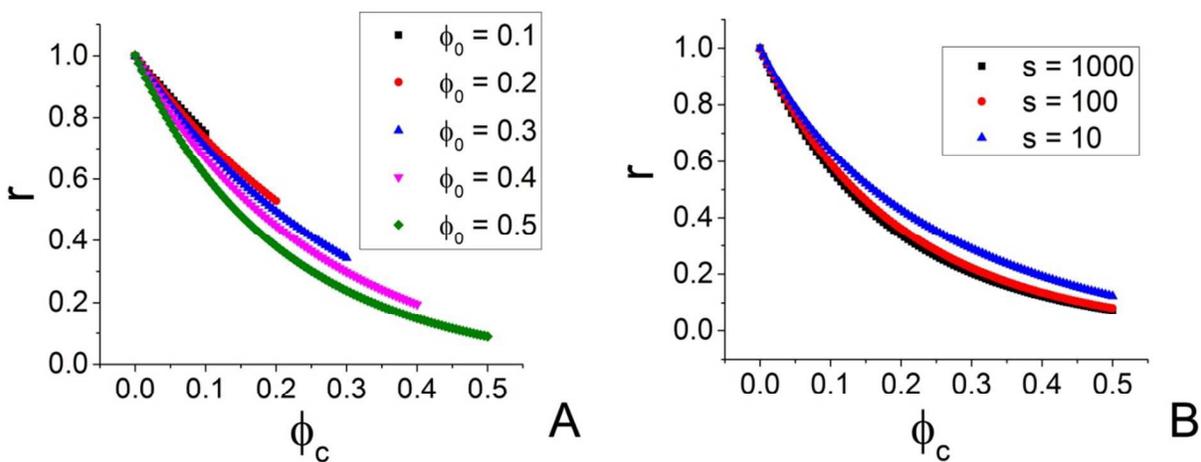


Fig.3 A: Plot of  $r$  against  $\phi_c$  at  $s=50$ , square:  $\phi_0=0.1$ , circle:  $\phi_0=0.2$ , upper triangle:  $\phi_0=0.3$ , lower triangle:  $\phi_0=0.4$ , diamond:  $\phi_0=0.5$ . B: fix  $\phi_0=0.5$ , square:  $s=1000$ , circle:  $s=100$ , triangle:  $s=10$ ;

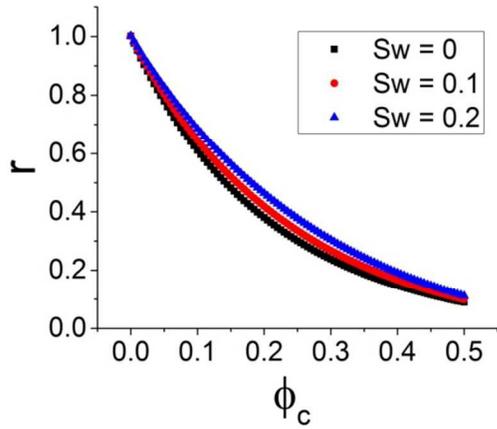


Fig.4 Plot of  $r$  against  $\phi_c$  with different degree of water incorporation. Square:  $S_w = 0$ , circle:  $S_w = 0.1$ , triangle:  $S_w = 0.2$ .

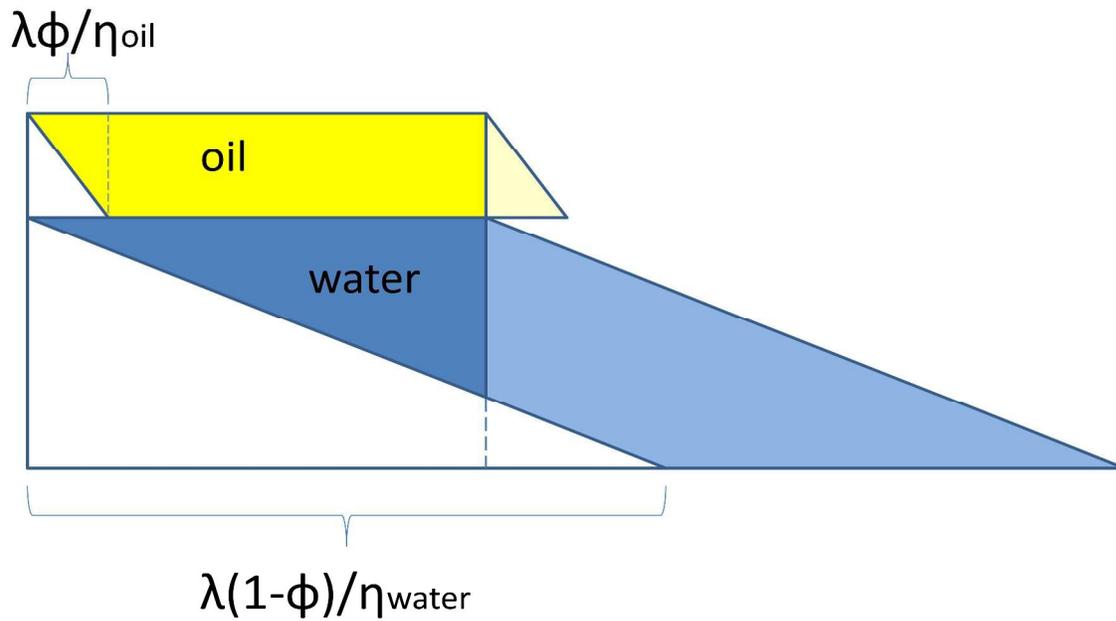


Fig.5 Schematic description of drainage. Dark blue: volume of water remained. Yellow: volume of water remained. Light blue: volume of water drained. Light yellow volume of oil drained.