Topical discussion notes - Thursday, January 10th, 2pm-3pm. Writing : D.Z.Gunes

Topic: Particles at interfaces – role of local versus global curvature in driving Ostwald ripening (or coarsening) – discussion of energy landscape for a particle as a function of its position at the interface

NB: This topic (or at least the part we discussed) could be discussed the same at the single bubble level or at the foam level, so it was discussed at the single bubble level.

1) **Initial question and introduction** : What is the role of local curvature in the rate/arrest of dissolution of a bubble covered by particles ? The mean curvature of the air/liquid interface sets the Laplace pressure difference between inside and outside the bubble, hence is the driving force for bubble dissolution or Ostwald ripening (see fig.1). Simulations with spherical particles (homogeneous surface, no roughness, not easily deformable) covering a bubble show that the air-liquid surface areas are flat when the free energy of the system is minimal (no reference given). The topic is nearly absent from the specialized literature. The discussion is relevant only to highly surface covered bubbles.

We all understand that as soon as the mean curvature of the air/liquid interface is 0, there is no longer a driving force for bubble size change. Is it necessary to fulfill this condition in order to stop bubble dissolution ? Or is the elastic modulus of the interface possibly a sufficient criterion in certain conditions ?

2) **Discussion**

-The pressure inside the bubble can even be set independently of the macroscopic curvature. It can be negative or positive (fig.1) with the same assembly of particles at the same positions.

-What sets the curvature is the volume of air taken up or given by the bubble. It thus appears that 0 mean local curvature would imply no driving force, but in many systems it does not seem necessary to stop bubble dissolution.

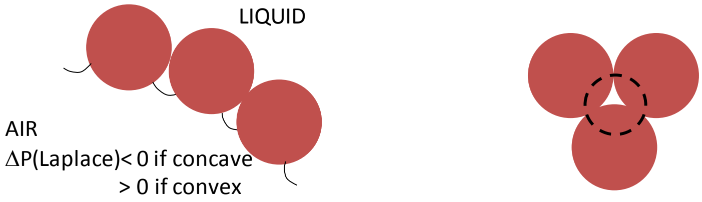

Fig.1. Illustration of importance of local curvature around a bubble in determining the Laplace pressure difference between air and liquid phases (left). In reality particles must build a viscoelastic percolated network to allow for such local curvature becoming independent from the global curvature; the curvature corresponds to the area designated by the dashed line circle (right).

-There seemed to be agreement to the idea that if we want to produce a purely mechanical criterion regarding the needed compressional modulus for stopping Ostwald ripening (following Gibbs), that would be : "the compressional modulus needs to have a finite value as zero frequency, which needs to be above a minimal value E_{min} (it was not discussed what the value E_{min} should be)". A short discussion on terminology took place : some express the criterion as "a jammed state of the interface is needed", others call that "a gel state" and others express it in terms of 2D rheology, i.e. "need of a yield stress in compression, i.e. the interface is a viscoelastic solid, with a minimal yield value" (solid does not mean that it should be continuous): the discussion did not emphasize real differences between these views/terminologies (though there may be). It was noticed that the criterion based on compressional deformation may not be sufficient (bending mode was mentioned to be actually very important as well). The term jamming may be more adequate to describe a relatively abrupt change in surface compressibility when reducing surface area.

So in conclusion to the initial question, it appeared that the gel interface with zero macroscopic tension is necessary and sufficient condition for stopping dissolution, whereas the zero mean local curvature is only a sufficient condition, not necessarily met in practice for particle-stabilized foams. It was pointed out that there could be saddle shapes at the air-liquid interface, i.e. due to particle roughness or non-spherical shapes. It was also remarked by several attendants that resistance to buckling (or bending) may be another necessary condition to stop Ostwald ripening, which can be in practice less easy than simply making a percolated interfacial layer. The reason is because if an interface can easily buckle, it could lose its gas without reducing its interfacial area. One important feature that may allow for larger bending resistance are higher lateral forces, such as present between hydrophobin type II particles adsorbed at air-water interface.

NB1: It was pointed out that in many systems, the compressional and the dilational linear viscoelastic moduli could be different. Both values are expected to be the same only for moduli arising from attractive interactions (see discussion in §3). The high enough modulus allows counteracting compressional forces due to Laplace pressure (capillary forces), and it is only if the macroscopic surface tension that can be measured in compression (e.g. using a Langmuir trough) can be brought to 0 that dissolution can be stopped. There seemed to be agreement as well to that idea.

NB2: An implication of the jammed interface, is that certain methods that are popular for measuring surface tension no longer apply. It is sometimes difficult to realize that, e.g. in the case of the rising bubble or similar methods, where the bubble shape can remain very nicely Laplacian (down to experimental resolution limit), but the method be completely irrelevant because of a jammed interface. In the case of jammed interface, stress at interface can be very heterogeneous. What matters is that the macroscopic surface pressure at the bubble scale can counter-balance surface tension due to the air-liquid interface.

The next part of the discussion was on the energy landscapes of particle-laden systems in “real” cases, where we know particles have significant roughness hence contact angle hysteresis.

3) Discussion extension : particle adsorption – free energy as a function of particle position at the interface – close to or far from lowest state of energy (considering only the 2D problem) ?

-Questioning the local curvature of the air-liquid interface between particles implies questioning as well the free energy of a particle at the interface and its dependence on the particle position. Do particles that attach the interface under mechanical agitation reach the lowest energy positions (or not very far), or can they be “trapped” in metastable positions rather far from the lower energy states.

-From this point on, we considered the case of particles having a certain type of roughness or chemical heterogeneities at their surface. Though not specified strongly at the time, the discussion mainly focused on particles of shape not too far from spheres. So does an equilibrium contact angle even exist in “real” cases i.e. with significant surface roughness or heterogeneity?

-The latter question comes from the remark that “real” surfaces always display large contact angle hysteresis, even when extreme efforts are put in order to suppress any kind of source of surface heterogeneity. Should one consider the advancing contact angle only or an average between advancing and receding ? The answer may depend on particle size as well.

-An introduction was given on the forces controlling adsorption depending on particle size and physic-chemical conditions. An overview is available in “Tchokalova et al., Phys Chem Chem Phys., vol.10, 1608

(2008)”. The importance of repulsive electrostatic forces between charged particles and air-water interface, or between particles and the particle-laden air-water interface, was first underlined. Evidence for that is e.g. the fact that the repulsion often needs to be reduced by increasing ionic strength in order to allow for particle adsorption and foaming. Large particles can be much better helped to overcome the energy barrier because they will be pushed by larger hydrodynamic force than small particles (under turbulent mixing). A consequence of the above mentioned effects is that particle roughness is in practice often key in facilitating particle adsorption.

-Some recent experimental results by Gunes et al. were described, that suggest that large particles may be subject to very slow dynamics at the interface, hence may stay a very long time far from an equilibrium contact angle (supposed to exist). They can be summarized as follows.

i)Experiments of particle adsorption from a suspension to air-water free surface were conducted with a variety of particle types (size ranging from 2 micron to 300 micron diameter), in a beaker under gentle magnetic stirring. Particle type was carboxyl latex (negatively charged surface) or glass beads. All systems showed progressive increase of number of particles attached at the interface as a function of time.

ii)The same experiment was conducted with a mixture of particles and SDS (c>cmc) : no particle attachment occurred.

iii)The next experiment was to inject SDS in the suspension after having covered the surface with a certain density of adsorbed particles. If stirring was absent, no desorption at all was observed. In the presence of stirring, complete desorption was observed over a typical time scale of the order of a couple of hours.

One possible explanation of these results may be that when injecting SDS to the system with pre-attached particles, absence of stirring may not allow for the change of particle position, because of the energy barrier to move the particle owing to its surface roughness (i.e. its contact angle hysteresis). If the particle was a smooth sphere with homogeneous surface, it would be pushed there progressively until finding, which was not observed. Hence, perturbation (mechanical, hydrodynamic) of the particles sitting the interface appear necessary to bring the particles to lower and lower energy states gradually. Until they fully desorb eventually, because of full wetting (or very small contact angle) which is the actual lowest state of energy - based on (ii).

-In another set of experimental results by Stoyanov et al., all particles were seen to reach close to their “equilibrium” contact angle as measured directly at the surface. The particles used were smaller than used in the study of Gunes et al. and the energy input was much higher - both conditions may play significant role. Observations by Stoyanov et al. plead for a view where particles do adsorb to go near the lowest energy position (at least in their experiments).

The very interesting debate about the necessary conditions to allow for reaching close to the lower energy position in the adsorption step could not reach very further, due to lack of either experimental or theoretical

-**The conclusion to §3** was that wetting dynamics (or hysteresis) may be very important in certain cases (larger particles, higher roughness) and not important in other cases (smaller particles or particles with very homogeneous surface). There is not much known in this problem.

Outlook question : can we force the mean curvature at the interface to 0 without bringing the macroscopic surface tension to 0 ?