

The relative energy of fcc and hcp foams

D. Whyte^{a*}, D. Weaire^a, W. Drenckhan^b and S. Hutzler^a

^a*School of Physics, Trinity College Dublin, Dublin 2, Ireland;* ^b*Laboratoire de Physique des Solides, Université Paris-Sud, CNRS UMR 8502, 91405 Orsay, France*

(Received 25 March 2015; accepted 20 May 2015)

The energies of face-centred cubic (*fcc*) and hexagonal close-packed (*hcp*) monodisperse foams, associated with their total surface area, are equal in the wet and dry limits, in the usual model. We prove that for all intermediate values of liquid fraction, *hcp* has lower energy. Energy considerations are thus not sufficient to explain the observed preference for crystallization into *fcc* over *hcp* in experiments using monodisperse bubbles.

Keywords: foams; emulsions

1. Introduction

The closely related face-centred cubic (*fcc*) and hexagonal close-packed (*hcp*) structures occur widely in materials science and idealized models; for example, in the crystal structures of many elements and in simulated hard sphere packings. Their relative energy (or in some cases the free energy) is always of interest as a determinant of the most stable structure. Such close-packed structures have been observed for monodisperse foams in recent years, with a distinct preference for *fcc* [1–3]. The structures form spontaneously when bubbles are produced using a flow-focusing device, which results in spherical bubbles with sub-millimetre diameters, smaller than the capillary length. The preference for *fcc* may be due to kinetics or fluid dynamics, or grain boundaries. It has also been attributed to a reduced mechanical stability of the *hcp* structure: the impact of rising bubbles onto a *hcp* arrangement can cause collapse [2].

Accordingly, the experiments do not simply imply that *fcc* must have a lower energy, which within the usual model for foams is equivalent to the surface area per bubble [4,5]. Nevertheless, we are drawn to examine the energy of each structure.

Here, we will offer an essentially rigorous proof that *hcp* has the lower energy for values of liquid fraction ϕ *between* its limiting values: the dry limit of $\phi = 0$ (although the structures are not stable in this limit, as discussed later) and the wet limit $\phi = \phi_c \approx 0.26$: the *critical liquid fraction* at which bubbles are spheres.

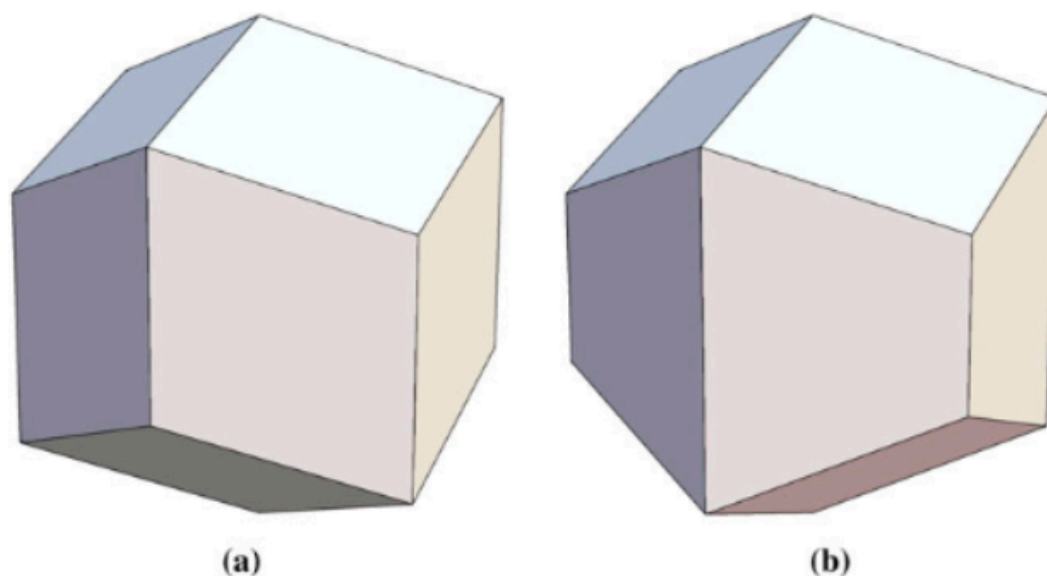


Figure 1. The shape of bubbles in the dry limit (i.e. $\phi = 0$). (a) fcc: a rhombic dodecahedron and (b) hcp: a trapezo-rhombic dodecahedron. All faces are flat and all the angles between adjoining faces are 120° , satisfying Plateau's conditions for equilibrium; however, these structures are unstable equilibria due to the presence of eightfold vertices.

2. Proof

In the wet limit ($\phi = \phi_c$), bubbles are perfect spheres, so clearly the energies of the two structures are equal. In the dry limit, a bubble in an fcc foam takes the form of a *rhombic dodecahedron*, with 12 identical rhombic faces; in hcp, a *trapezo-rhombic dodecahedron*, with 6 rhombic and 6 trapezoidal faces, as in Figure 1. These polyhedra have identical surface areas so the energies are also equal at $\phi = 0$.

For all liquid fractions, we assume a canonical foam, in which the bubble surface assumes a unique shape which minimizes its surface area at constant volume. We assume that in the ordered structures discussed, each bubble possesses all the symmetries of the underlying lattice.

Figure 2a shows the form of a bubble in equilibrium for a fcc foam between the wet and dry limits, at $\phi \approx 0.125$. Also indicated is a plane, which divides the bubble into two pieces. Since the fcc lattice is centrally symmetric, any plane passing through the centre of the bubble divides its surface into two congruent pieces, equal in area and volume: we use the (1 1 1) plane, indicated by the dashed lines in Figure 2. We can reflect one half of the fcc surface (the top half in the figure) in this dividing plane to obtain the form shown in Figure 2b. This new surface is everywhere continuous and retains the surface area and volume of fcc, but its planar contacts match the hcp structure. It may be regarded as a trial solution for hcp, and cannot therefore have a lower energy. Indeed the energy must be *higher*, since this rejoining results in discontinuities in the surface normal (see exaggerated sketch in Figure 3). Hence the surface can be relaxed, removing these 'kinks' and lowering its energy. This completes the proof. Such rigorous proofs are quite rare in this subject (see e.g. [6]).

Preliminary simulations using the Surface Evolver [7] confirm that there is indeed a very small but detectable difference in the energies of bubbles in fcc and hcp foams, of the order

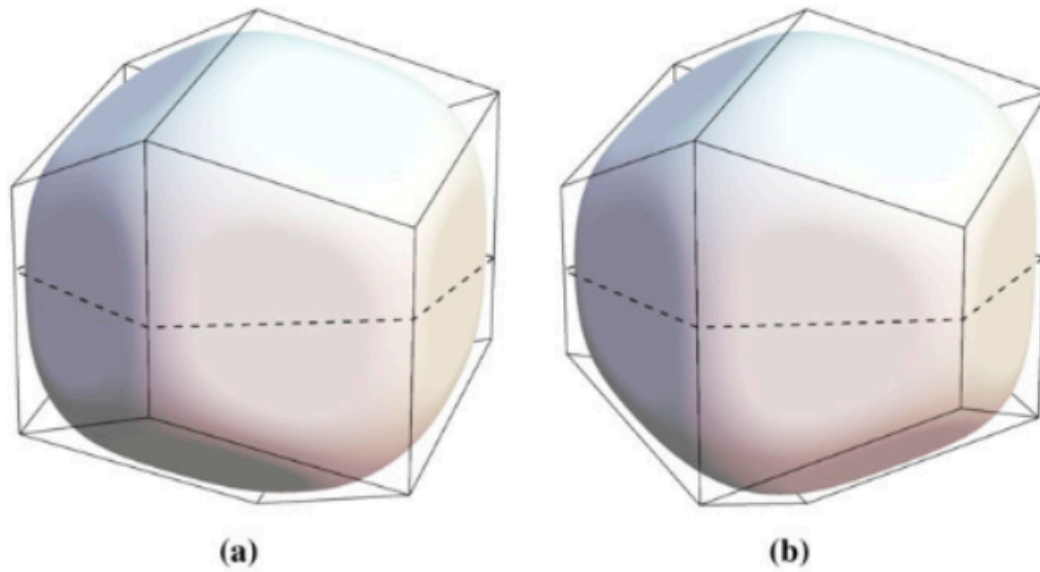


Figure 2. (a) shows a bubble in an fcc foam at liquid fraction $\phi \approx 0.125$, obtained from a Surface Evolver simulation. (b) is obtained by reflecting the top half of the fcc bubble in a dividing plane (dashed line). This results in a trial solution for hcp.

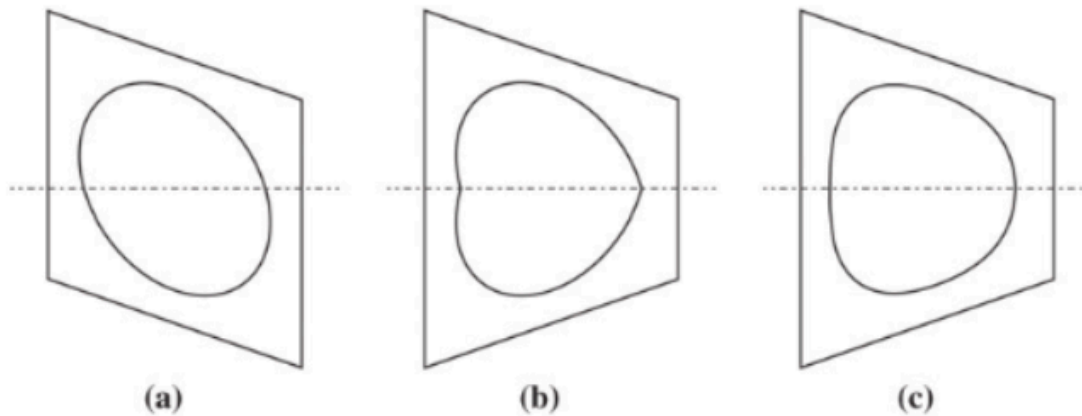


Figure 3. The surface obtained by reflection in Figure 2b is continuous but not smooth: it can be further relaxed to obtain a surface of lower energy. Here (a) shows the shape of the flat contact for an fcc bubble, (b) for the trial hcp surface and (c) the further relaxed hcp surface. The kink has been exaggerated here for clarity.

of $10^{-3}\%$. These simulations will be reported in detail in a further publication, together with order-of-magnitude estimates of the energy difference, relating it to the relaxation described in Figure 3.

3. Discussion

The hcp structure has an extra degree of freedom, in that its axial ratio c/a (i.e. twice the ratio of the separation of close-packed planes to the separation of neighbouring bubbles within the planes) is not fixed by symmetry. In the wet limit, spherical bubbles ensure the ideal close-packed ratio of $\sqrt{8/3}$. In the dry limit, it is easy to show that the surface area of

the trapezo-rhombic dodecahedron described earlier is minimized in the ideal axial ratio. For intermediate values of ϕ this does not hold. If indeed varying c/a from its ideal value does result in a reduction of the energy of an hcp foam, this only strengthens our result.

Due to the symmetry of the fcc lattice, all contacts between fcc bubbles are planar for any liquid fraction. The same argument applies only to 6 of the 12 contacts for an hcp bubble (those which are trapezoidal in the dry limit). It follows that it may be possible to further lower the energy of an hcp bubble by allowing the other faces (those which are rhombic in the dry limit) to warp slightly. Again, this does not affect our result, since it can only result in a further reduction of the energy of hcp.

We should also note that the fcc and hcp structures are unstable very close to the dry limit, due to the instability of junctions of more than four Plateau borders (i.e. liquid channels) in the dry limit [8,9]. Instead, the body-centred cubic or ‘Kelvin structure’ tends to occur in ordered dry foams [10,11]. This does not affect our calculations – we deal only with a single bubble in a fixed fcc environment and so no such instability arises. It is also worth noting that experimentally, mixtures of fcc and hcp arrangements are seen when close-packed planes are randomly stacked. However, in this case, each bubble can be considered locally to be either fcc or hcp, depending on the positions of its nearest neighbours.

It is tempting to consider a similar inverse argument, in which half of an hcp bubble is ‘twisted’ by 30° and rejoined to yield an fcc bubble of equal surface area. This argument fails: the intersection of the hcp bubble with the dividing plane has only threefold rotational symmetry and so this process results in a discontinuous surface.

In summary, we have shown that the energy of an fcc foam slightly exceeds that of an hcp foam for liquid fractions $0 < \phi < \phi_c$, with equality at $\phi = 0$ and $\phi = \phi_c$. The experimentally observed preference for fcc over hcp can thus not be attributed to energy differences. Further details of relevant simulations will be provided in a subsequent publication.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This publication has emanated from research supported in part by a research grant from Science Foundation Ireland (SFI) [grant number 13/IA/1926]; MPNS COST Actions MP1106 ‘Smart and green interfaces’ and MP1305 ‘Flowing matter’ and the European Space Agency (AO-09-943, AO-99-108, AO-09-813, AO-99-075); the European Research Council (ERC) under the European Union’s Seventh Framework Program (FP7/2007-2013) in the form of an ERC Starting Grant, agreement 307280-POMCAPS.

References

- [1] A. Van der Net, W. Drenckhan, D. Weaire and S. Hutzler, *Soft Matter* 2 (2006) p.129.
- [2] S. Heitkam, W. Drenckhan and J. Fröhlich, *Phys. Rev. Lett.* 108 (2012) p.148302.
- [3] A. Meagher, D. Whyte, J. Banhart, S. Hutzler and F. Garcia-Moreno, *Soft Matter* 11 (2015) p.4710.
- [4] D. Weaire and S. Hutzler, *Foams*, in *The Oxford Handbook of Soft Condensed Matter*, M. Eugene and D. Weitz, eds., Oxford University Press, Oxford, 2015 p.147.

- [5] I. Cantat, S. Cohen-Addad, F. Elias, F. Graner, R. Höhler and O. Pitois, *Foams: Structure and Dynamics*, Oxford University Press, Oxford, 2013.
- [6] R. Kusner and J.M. Sullivan, *Forma* 11 (1996) p.233. Reprinted in *The Kelvin Problem*, Taylor & Francis, London, 1996, p.71 .
- [7] K.A. Brakke, *Exp. Math.* 1 (1992) p.141.
- [8] D. Weaire, N. Pittet, S. Hutzler and D. Pardal, *Phys. Rev. Lett.* 71 (1993) p.2670.
- [9] K. Brakke, *Colloids and Surfaces A: Physicochem: Eng. Aspects* 263 (2005) p.4.
- [10] D. Weaire, *The Kelvin Problem*, Taylor & Francis, London, 1997.
- [11] R. Höhler, Y. Yip Cheung Sang, E. Lorenceau and S. Cohen-Addad, *Langmuir* 24 (2008) p.418.