Electronic Supplementary Information for Soft Matter manuscript:
The energy of fcc and hcp foams.

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SUPPLEMENTAL MATERIAL

S1 Variation of Plateau border radius between two nodes for the case of a Kelvin foam

In subsection 5.2.1 we have derived a functional form for the variation of the Plateau border radius $r(x)$ between two nodes in a dry foam. We have tested the applicability of this form using Surface Evolver data for the familiar case of a Kelvin foam, in which all nodes are of the tetrahedral type. In this case eqn. (18) reduces to

$$\delta(x) = 2\alpha e^{-\frac{L}{2c_1 r_0}} \cosh\left(\frac{x-L}{2c_1 r_0}\right). \qquad \text{(S-1)}$$

Figure S1 shows numerical Surface Evolver data for the longitudinal variation of Plateau border radius $r(x)$ for liquid fraction $\phi = 0.01$ and $\phi = 0.04$, respectively. Away from the two nodes the data is well described by the functional form of eqns. (15) and (S-1).

The fitted value for the node constant α depends critically on the value of L in eqn. (18). Taking L as the edge length of a Kelvin foam would for our simple model lead to an overlap of the Plateau borders close to a node. We may define a shortened effective Plateau border length via the meeting point of two Plateau borders, as modelled by eqn. (15). The shortening is then given by $2\Delta_\alpha$, with $\Delta_\alpha = r_0(1+\alpha)/(\alpha/c_1 + \sqrt{3}\tan(\theta_\alpha/2))$, where $\theta_\alpha = \arccos(-1/3) = 109.47^o$ is the vertex angle in the Kelvin foam.

A least square fit of the Plateau border profile then results in $\alpha \simeq 0.9$. This value is roughly consistent with the estimate of $\alpha \simeq 0.56$, as obtained from the variation of excess energy with liquid fraction, see Appendix S2.3. A fit without the above length correction results in $\alpha \simeq 2.5$.

Estimate of node constants can in principle also be obtained from approximations of the vertex geometry, but we have not pursued this.

S2 Evaluation of constants in the energy expansions of dry foams

We will in the following evaluate the numerical constants E_{dry}, E_1, E_2 and E_3 in the energy expansion of eqn. (23), i.e.

$$E(\phi)/(4\pi R^2) = E_{dry} - E_1\sqrt{\phi} + E_2\phi\left(1 - \exp\left[-E_3/\sqrt{\phi}\right]\right), \qquad \text{(S-2)}$$

for the cases of a single bubble of volume $\frac{4}{3}R^3\pi$ arranged in an fcc foam (S2.1) and in a Kelvin (S2.3) foam, respectively. We will use the lowest order expression eqn. (19) to relate liquid fraction ϕ to the asymptotic Plateau border radius r_0; we rewrite this as

$$r_0(\phi) = \frac{L}{\sqrt{\lambda c_g}}\sqrt{\phi} \qquad \text{(S-3)}$$

with geometrical constants $c_g = \sqrt{3} - \pi/2$, $\lambda = 3/(2\sqrt{2})$ (Kelvin), $\lambda = 9/(2\sqrt{3})$ (fcc,hcp), L is the edge length of the corresponding dry foam polyhedron of volume $\frac{4}{3}R^3\pi$.

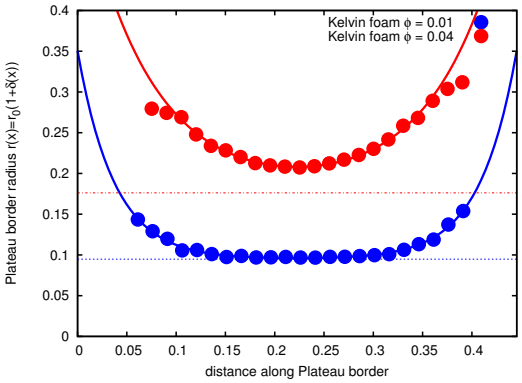

Fig. S1 Variation of Plateau border radius $r(x) = r_0(1+\delta(x))$ between two vertices in a Kelvin foam at liquid fraction $\phi = 0.01$ and $\phi = 0.04$. The data points are from Surface Evolver calculations (bubble volume 1), the solid line is a fit to eqns. (15) and (S-1), resulting in an estimate $\alpha \simeq 0.9$. The dashed lines indicate the respective values of r_0.

Using the area reduction per Plateau border, eqn. (20), we obtain

$$\Delta a_L(\phi)/(4\pi R^2) = -\frac{2\sqrt{3}-\pi}{4\pi\sqrt{c_g\lambda}}\left(\frac{L}{R}\right)^2\sqrt{\phi}. \qquad \text{(S-4)}$$

The correction term (per Plateau border) due to the presence of the nodes, eqn. (22), may be written as a function of liquid fraction ϕ,

$$\Delta n_{L,\alpha,\beta}(\phi)/(4\pi R^2) = \frac{2\sqrt{3}-\pi}{4\pi}\frac{c_1}{\lambda c_g}\left(\frac{L}{R}\right)^2 \times \\ \times(\alpha+\beta)\phi\left(1 - \exp\left[-\frac{\sqrt{\lambda c_g}}{c_1\sqrt{\phi}}\right]\right). \qquad \text{(S-5)}$$

In the following we will evaluate the above expressions for both a bubble in an fcc foam (S2.1), and in a Kelvin foam (S2.3).

S2.1 Energy per bubble in an fcc foam

The volume of a rhombic dodecahedron of side length L is given by $V = 16\sqrt{3}/9L^3$, resulting in $L/R = \left(\frac{\pi\sqrt{3}}{4}\right)^{1/3}$. The surface area is $A = (8\sqrt{2})L^2$, leading to the normalised dry foam energy $E_{dry} = A/(4\pi R^2) = \frac{8\sqrt{2}}{4\pi}(L/R)^2 \simeq 1.10534$ for an fcc cell with flat faces.

In an fcc foam there are 24/3=8 Plateau borders per bubble. From eqn. (S-4) the first energy correction term is thus given by $8\Delta a_L(\phi)/(4\pi R^2) = E_1\sqrt{\phi}$ with $E_1 \simeq -0.3894$.

Each Plateau border connects two different types of nodes, corresponding to the vertex angles $\theta_\alpha = \cos^{-1}(-1/3) \simeq 109.47^o$ and $\theta_\beta = \cos^{-1}(1/3) \simeq 70.53^o$. The node correction *per bubble* is thus given by $8\Delta n_{L,\alpha,\beta}(\phi)$, see eqn. (S-5). This results in the final form for the node correction as $E_2\phi(1 - e^{-E_3/\sqrt{\phi}})/(4\pi R^2)$ with $E_2 \simeq 0.305(\alpha+\beta)$ and $E_3 = \sqrt{c_g\lambda}/c_1 \simeq 1.646$, where the sum $\alpha+\beta$ needs to be determined from a one-parameter least square fit.

Figure 12 shows the Surface Evolver result for the excess energy of a bubble in an fcc foam bubble, $\varepsilon(\phi) = E(\phi)/(4\pi R^2\gamma) - 1$, as a function of liquid fraction ϕ. The data is well described by the one parameter fit to the energy expansion of eqn. (S-2), resulting in $\alpha+\beta = 1.29 \pm 0.02$.

Inserting $\alpha \simeq 0.9$ (from the fit of the Plateau border profile for a Kelvin foam, Appendix S1) results in $\beta \simeq 0.4$; inserting $\alpha \simeq 0.56$

(from the value obtained for the energy of a Kelvin foam, S2.3) results in $\beta \simeq 0.7$.

S2.2 Energy difference between fcc and hcp foams

The calculation of the node correction for a bubble in the hcp structure is slightly more elaborate. Of its 24 edges, 18 are identical to those in fcc, while 3 edges have an α node at each end and length $\frac{4}{3}L$, and the remaining 3 edges have a β node at each end and length $\frac{2}{3}L$. This results in the following node correction per bubble, $\frac{1}{3}\left(18\Delta n_{L,\alpha,\beta)}(r_0) + 3\Delta n_{\frac{4}{3}L,\alpha,\alpha}(r_0) + 3\Delta n_{\frac{2}{3}L,\beta,\beta}(r_0)\right)$.

The difference per bubble between the fcc and hcp node corrections is then readily computed as $2\Delta n_{L,\alpha,\beta} - \Delta n_{\frac{4}{3}L,\alpha,\alpha}(r_0) - \Delta n_{\frac{2}{3}L,\beta,\beta}(r_0)$.

Inserting for the node correction terms *per Plateau border*, Δn, eqn. (22), and using eqn. (19)) for relating r_0 to ϕ results in the following expression for the energy difference between fcc and hcp as a function of liquid fraction ϕ,

$$(E_{fcc}(\phi) - E_{hcp}(\phi))/(4\pi R^2) = E_4\phi \exp\left[-E_3/\sqrt{\phi}\right] \times \\ \times \left[\alpha\left(\exp\left[-E_3/(3\sqrt{\phi})\right] - 1\right) + \beta\left(\exp\left[+E_3/(3\sqrt{\phi})\right] - 1\right)\right]. \quad \text{(S-6)}$$

The constants are given by $E_3 = \sqrt{c_g\lambda}/c_1 \simeq 1.646$ (the value of E_3 for the fcc foam) and $E_4 = \frac{2\sqrt{3}-\pi}{\pi}\frac{c_1}{\lambda c_g}\left(\frac{L}{R}\right)^2 \simeq 0.059$.

A two-parameter fit to eqn. (S-6) is shown in figure 13, resulting in $\alpha = 0.82 \pm 0.02$ and $\beta = 0.20 \pm 0.01$. This is roughly consistent with the values obtained in the other estimates, see table 1.

S2.3 Kelvin foam

S2.3.1 Energy

The volume of Kelvin's tetrakaidecahedron of side length L is given by $V = 8\sqrt{2}L^3$, resulting in $L/R = \left(\frac{\pi}{6\sqrt{2}}\right)^{1/3}$. The surface area is $A = (6+12\sqrt{3})L^2$, leading to the normalised dry foam energy $E_{dry} = A/(4\pi R^2) = \frac{6+12\sqrt{3}}{4\pi}(L/R)^2 \simeq 1.0990$ for a Kelvin cell with flat faces. Energy minimisation using the Surface Evolver results in $E_{dry} \simeq 1.09725$.

In a Kelvin foam there are 12 Plateau borders per bubble. From eqn. (S-4) the first energy correction term is thus given by $12\Delta a_L(\phi)/(4\pi R^2) = E_1\sqrt{\phi}$ with $E_1 \simeq -0.384$.

In the Kelvin structure all vertex angles are identical, the energy correction due to the nodes is thus given by $12\Delta n_{L,\alpha,\alpha}(\phi)$, see eqn. (S-5). This results in the final form for the node correction as $E_2\phi(1-e^{-E_3/\sqrt{\phi}})/(4\pi R^2)$ with $E_2 \simeq 0.183\alpha$ and $E_3 = \sqrt{c_g\lambda}/c_1 \simeq 1.051$, where the node constant α needs to be determined from a least square fit.

Figure S2 shows the Surface Evolver result for the excess energy of a Kelvin bubble, $\varepsilon(\phi) = E(\phi)/(4\pi R^2\gamma) - 1$, as a function of liquid fraction ϕ. The data is well described by the one-parameter fit to the energy expansion of eqn. (S-2) over the entire range of stability of this structure. The value of the node constant $\alpha \simeq 0.56$, is lower than the estimate of this constant as obtained from fitting the Plateau border profile ($\alpha \simeq 0.9$, see Figure S1).

S2.3.2 Further estimate of node constant α

There is yet a further route for establishing a value of the node constant α in a Kelvin foam. Phelan *et al.*[36] obtained an expression for ϕ as a function of r_0 from a Surface Evolver computation of the volume of a single four-fold node, i.e. the node of the Kelvin

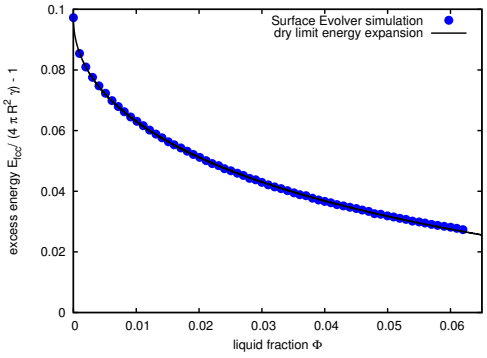

Fig. S2 Excess energy $\varepsilon(\phi) = E(\phi)/(4\pi R^2\gamma) - 1$ as a function of liquid fraction ϕ for a bubble in a Kelvin structure. The black line results from a one-parameter fit to the dry limit energy expansion, eqn. (S-2), resulting in the node-constant $\alpha \simeq 0.56 \pm 0.01$.

structure. A more accurate result (obtained in the same way) is due to Koehler *et al.*[37] who obtained,

$$\phi = \lambda c_g (r_0/L)^2\left(1 + 1.17\frac{r_0}{L}\right), \quad \text{(S-7)}$$

with $\lambda = 3/(2\sqrt{2})$ for the Kelvin structure, see section S2.

Such a relation may also be obtained from

$$\phi = \lambda c_g L^{-2}\langle r^2(x)\rangle = \lambda c_g L^{-1}\int_0^L r^2(x)dx, \quad \text{(S-8)}$$

with $r(x) = r_0(1+\delta(x))$. Evaluating the integral to lowest order in $\delta(x)$ results in

$$\phi = \lambda c_g (r_0/L)^2\left(1 + \frac{2}{L}\int_0^L \delta(x)dx\right), \quad \text{(S-9)}$$

and thus

$$\phi \simeq \lambda c_g (r_0/L)^2\left(1 + 4c_1\alpha\frac{r_0}{L}\left(1 - \exp\left[-L/(c_1 r_0)\right]\right)\right) \simeq \\ \simeq \lambda c_g (r_0/L)^2\left(1 + 4c_1\alpha\frac{r_0}{L}\right) \quad \text{(S-10)}$$

Comparing with the expression by Koehler *et al.*[37], eqn. (S-7), we can thus identify $4c_1\alpha = 1.17$. This leads to $\alpha \simeq 0.75$, again consistent with the other estimates for α reported above.