Comment on Biomimetic Ultrathin Whitening by Capillary-Force-Induced Random Clustering of Hydrogel Micropillar Arrays

Chandra et al. (1) calculate the typical cluster size ξ of micropillars that are immersed in water and cluster because of the capillary interaction induced by the liquid−vapor interface of the evaporating water. These authors correct mistakes in similar calculations carried out previously by other authors (2–4). However, all these papers share, explicitly or implicitly, a common flaw.

The size ξ of a cluster follows from energy minimization. The energy $U_{cluster}$ consists of two contributions: (i) the elastic energy U_e of bending the pillars and (ii) the capillary energy U_c due to the presence of the liquid−vapor interface. The authors calculate these two energies for a cluster of N pillars in order to obtain the total energy of a cluster $E_{cluster}(N)$ followed by calculating the number N_c of pillars that minimizes this expression. However, it is the total energy which must be minimized, not the energy of a single cluster. Assuming that every pillar belongs to a cluster and that all clusters have the same size N, the total energy is $U_{total}(N) = N_{clusters}U_{cluster}(N)$, where $N_{clusters}$ is the number of clusters in the system. This is $N_{clusters} = N_{total}/N$, i.e., the total number N_{total} of pillars divided by the number N of pillars in each cluster. So the energy that needs to be minimized is $(N_{total}U_{cluster}(N))/N$, not $U_{cluster}(N)$.

We use for the energy $U_{cluster}(N) = U_e(N) + U_c(N)$ of a cluster the expressions for U_e and U_c of Chandra et al. (1) (eqs 7 and 9, respectively, therein). We provide a critical assessment of the reasoning leading these authors to obtain explicit expressions for U_e and U_c (for more details, see the original paper (1)). For a square lattice of posts, the clusters collapse with the symmetry of this lattice and have n "layers" or perimeters (1). The bending energy of a cylindrical post of height h, radius r, and Young's modulus E is

$$E_b = \frac{3\pi E r^4 \delta^2}{8h^3} \tag{1}$$

where δ is the displacement of the free end of the post. The total bending in the jth perimeter is

$$\delta_j^2 = 4\left(\frac{s}{2}\right)^2[(2j-1)^2 + (2j-1)^2] + 8\left(\frac{s}{2}\right)^2\sum_{i=1}^{j-1}[(2j-1)^2 + (2i-1)^2] \tag{2}$$

where s is the interpost wall-to-wall distance. The first term stems from the bending of the four corner posts and the second term stems from the remaining posts in the perimeter. Thus the total bending of a cluster of n perimeters is (5)

$$\delta^2 = \sum_{j=1}^{n}\delta_j^2 = \frac{s^2}{3}(8n^4 - 2n^2) \tag{3}$$

From eqs 1 and 3 the total elastic energy of a cluster is (6)

$$U_e = \frac{\pi E r^4 s^2 (8n^4 - 2n^2)}{8h^3} \tag{4}$$

where the total number of posts N is given by $N = 4n^2$. The accuracy of this result depends, of course, on the degree to which the assumptions used are valid, i.e., that linear elastic theory describes the bending of the posts (not valid for large bending) and that the clusters are indeed formed by "layers" of posts and are neatly arranged in a superlattice. In the following, the question as to which degree these assumptions are valid will not be pursued further, but this will be important for future more detailed analyses.

The capillary energy between two vertical cylindrical posts partially submersed in a liquid of surface tension σ and separated by a center-to-center distance $2l$ is given by

$$W = 2\pi\sigma r^2\cos^2\theta\left(\ln\frac{(a+l)\gamma_e q}{1+\sin\theta}\right) \tag{5}$$

where θ is the contact angle of the liquid with the posts, $\gamma_e = \exp(\gamma) = 1.78107$, is the exponential of the Euler−Mascheroni constant γ, $a^2 = l^2 - r^2$, and $q^{-1} = \sqrt{\sigma/(\rho g)}$ is the capillary length, with ρ the mass density of the liquid and g the gravitational acceleration. Considering the interaction of each post with the surrounding eight posts, the total energy change due to the capillary energy for a cluster of n perimeters is (7)

$$U_c = -4\pi\sigma r^2\cos^2\theta\left[(4n^2 - 2n + 3)\ln(\sqrt{3}+2) + (4n^2 - 4n + 1)\ln\left(\frac{\sqrt{7}+2\sqrt{2}}{\sqrt{2}+1}\right)\right] \tag{6}$$

The accuracy of this calculation is also dependent on the validity and consideration of several assumptions and effects, respectively: (i) The above expression ignores capillary interactions between posts in different clusters. (ii) The interaction between posts other than just the surrounding eight posts assumed above can be important for the energy of the clustered state. (iii) The capillary interaction is a many-body interaction and this can also be important for the energy of the clustered state. (iv) Finally, eq 5 is not valid for posts close to contact and once again the energy for the clustered state can be different. The accurate calculation of the capillary interaction without the above assumptions is a very difficult problem and we do not consider it further. As before, these effects will be important for future more detailed studies.

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From the minimization of $(N_{total}U_{cluster}(N))/N$, we obtain the relation

$$\frac{4h^3\sigma\cos^2\theta}{ER^2s^2} = \frac{n_c^3}{(1 - 3/n_c)\ln(\sqrt{3} + 2) + (2 - 1/n_c)\ln\left(\frac{\sqrt{7} + 2\sqrt{2}}{\sqrt{2} + 1}\right)} \quad (7)$$

Using this relation for large n_c (i.e., for large h or small E) we can compare directly with the published results. We find $\xi \propto h$ and, because of $N_c \propto \xi^2$, $N_c \propto E^{-2/3}$. These results are to be compared with the predictions $\xi \propto h^{3/2}$ and $N_c \propto E^{-1}$ as obtained by Chandra et al. (1) upon minimizing $U_{cluster}(N)$ only.

Moreover, it is a relevant issue whether the system can actually reach this energy minimum. The typical energy scale σR^2 is much bigger than k_BT so that thermal fluctuations are not able to drive the system into the global energy minimum. Clustering is probably more of a dynamic, history-dependent process akin to coalescence as studied by Py et al. (8). These authors obtain $\xi \propto h^{4/3}$ and their results imply $N_c \propto E^{-2/3}$. The relevance of dynamics for these issues has also been clearly discussed by Pokroy et al. (9). A complete understanding of this more complex process will require further, more detailed, and complete theoretical analysis and experimental validation.

The experimental results of Zhao and Fan (3) indicate $\xi \propto h^{1.2}$ (six data points) and those of Chandra et al. (1) indicate $N_c \propto E^{-1}$ (three data points). In view of these experimental results and the three different sets of theoretical predictions described above, it would be interesting if Chandra et al. (1) could reanalyze their data and thus help to clarify this issue.

REFERENCES AND NOTES

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