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

In their comment on our earlier paper (1), Bernardino et al. (2) raised an interesting question, that is, which relevant energy should be minimized to obtain the cluster size of the micropillars assembled by capillary force. By minimizing the total energy, rather than the energy of a single cluster, they obtained the scaling of cluster size N_c with the micropillar elastic modulus E as $N_c \sim E^{-2/3}$, the same as that implied by Py et al. (3) but different from the $N_c \sim E^{-1}$ scaling that we obtained by minimizing the energy of a single cluster (1) similar to Zhao et al. (4) Although we agree that in the case of *ultra*-high-aspect-ratio fibrous structures, minimization of the total energy is relevant, we argue that in the case of relatively short pillars, such as ours, it is indeed the energy of a single cluster rather than the total energy that should be minimized to obtain the cluster size.

Minimization of the total energy as suggested by Bernardino et al. (2) implies that the clusters once formed can interact and rearrange to achieve the minimum energy for the whole system. This may be true for ultra-high-aspect-ratio fibers, such as those shown by Py et al. (3) (aspect-ratio $(L_N/2b) > 140$ for which data is reported in their Figure 6), where clusters coalesce in a self-similar fashion to achieve a final configuration. In our experiments, pillars have modest aspect ratios (12 for geometry A and 9 for geometry B), and the clusters grow by joining of additional pillars at the periphery. Once formed, the clusters cannot rearrange or bend collectively because of irreversible interpillar adhesion and high effective bending stiffness of the cluster respectively. Under these conditions, the system cannot reach the global energy minimum as Bernardino et al. (2) doubted. To derive the scaling of the cluster size, an equivalent approach is to determine the critical cluster size N_c at which it becomes energetically unfavorable for an additional pillar to join the cluster. The bending energy E_b of the additional pillar joining a cluster scales as $E_b \sim E\delta^2$, where δ is the deflection required for the pillar to join a cluster of size N and scales as $\delta \sim \sqrt{N}$. Thus the bending energy scales as $E_b \sim EN$. Because the capillary energy reduction E_c of the additional pillar joining the cluster is independent of cluster size N, equating E_b and E_c readily gives the scaling for N_c as $N_c \sim E^{-1}$. Replotting our data shown in Figure 4 (1) in the form of *l*og N vs log E plot yields slopes of -1.0 ± 0.1 for micropillars in geometry A and -1.2 ± 0.2 for those in geometry B, both of which are close to -1. In symmetric arrays as ours, the pillars are initially in equilibrium with zero net lateral capillary meniscus force. However, the equilibrium is unstable and a small perturbation of a single pillar would result in net attractive force on the perturbed pillar, starting the clustering process.

The assumption of no cluster bending can be verified by estimating the critical modulus of stability for a cluster (5). Assuming interpillar adhesion, the bending stiffness and thus the elastic restoring force (eq 8 in ref 5.) of a cluster scales as $\sim N^2$, whereas the capillary force (eq 7 in ref 5) scales as $\sim N^{1/2}$. Thus, the critical elastic modulus (eq 9 in ref 5), $E_{\mathrm{crit}}^{N} = N^{-3/2} E_{\mathrm{crit}}^{1}$, where superscripts denote cluster size. The lowest elastic moduli for which the cluster sizes are plotted in Figure 4 (1) are greater than that estimated from the above equation for both the geometries even for the smallest clusters ($N = 4$), which prevents coalescence of clusters by bending. Experiments over a range of elastic modulus with sufficiently high-aspect-ratio pillars and no interpillar adhesion would allow for cluster bending and rearrangement and should reveal $N_c \sim E^{-2/3}$ for lower moduli before crossing over to $N_c \sim E^{-1}$ scaling for higher moduli.

We point out that the capillary driving force responsible for clustering in the system reported by Py et al. (3) is quite different from ours and that reported by Zhao et al. (4) In our later publication (5), we detailed the different types of capillary forces that are responsible for clustering of tall structures. Specifically, in the case of Py et al. (3), the capillary attraction between fibers is due to reduction in liquid−air interface along the fiber length and thus the capillary energy depends on the fiber length, whereas in ours (1) and that of Zhao et al. (4), the capillary meniscus interaction energy is responsible for clustering, which is independent of the pillar height h. Moreover, in the case of Py et al. (3), bending length is chosen by the clustering process whereas in ours and Zhao et al. (4), it is fixed. Therefore, there are different scalings of cluster dimension ξ ($\xi \sim \sqrt{N_c}$) vs h as pointed out by Bernardino et al.: $\xi \sim h^{3/2}$ in ours (1) and that of Zhao et al. (4) results from the minimization of single cluster energy where capillary energy is independent of h; $\xi \sim h$ obtained by Bernardino et al. (2) results from the minimization of total energy where capillary energy is independent of h; and $\xi \sim h^{4/3}$ by Py et al. (3) because capillary energy is dependent on h. The fact that Zhao et al. (4) experimentally obtained $\xi \sim h^{1.2}$ in bundled Si nanorods, where the exponent 1.2 lies between 1 (prediction by Bernardino et al. (2) by minimizing total energy) and 1.5 (our prediction by minimizing single cluster energy), suggests that some intercluster rearrangement (typical micropillar aspect ratio of ∼30 estimated from the base diameter of the pillars (6)) may contribute to some extent toward minimization of total energy.

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