Dear Sirs,

We wish to appeal the rejection of our paper LX9360, “Surface Driven Bulk Reorganization of Gold Nanorods”, to a Divisional Associate Editor. We have received reviews from three referees. Referee B is in favor of publication in PRL. Referees A and C are opposed, however they reject publication for completely contradictory reasons. Referee A rejects because he believes our main conclusion, relating the global shape stability of a nanometer sized rod to the roughening of its exposed surfaces, is obvious. Referee C rejects because he believes this very same conclusion is wrong. Such a direct conflict of opinions, from referees who are presumably experts in the field, indicates to us that the situation is far from clear, and that our paper can therefore make a significant contribution. We therefore request further consideration. Below we give our detailed reply to the last comments of the referees A and C, and indicate the changes we have made to our manuscript in response.

Reply to referee A

Referee A argues that the well known theory of equilibrium shapes explains and predicts our main results. He rejects our work stating that we have failed to discuss our results “in the context of the well studied field of crystal shape physics”. We disagree. Firstly, we are well aware the theory of equilibrium shapes. Indeed one of us (Teitel) is a co-author on the very first paper (now our Ref. [2], earlier was Ref.[13]) to relate the faceting transition of equilibrium shapes to the roughening transition of the corresponding surface within a model that goes beyond the earlier mean field theories. Our discussion in the 4th paragraph from the end is specifically motivated by these ideas. It is ironic that our mention in this paragraph of roughening, as the likely mechanism for nucleating shape change, is what leads referee C to reject our paper.

The papers by Metois et al. that referee A cites, are nice experimental works that show that micron sized crystallites of Au and Pb can achieve their equilibrium shape, when starting from very different initial configurations and annealed for long times at high temperatures (above the {110} roughening temperature). However, it is not obvious to extrapolate results from micro to nano sized objects. The theory of equilibrium shapes applies, in principle, to the limit of an object large enough that the thermodynamic limit applies. One considers only minimization of the surface free energy and ignores excitations in the bulk of the material. Evolution into the equilibrium shape in such systems is assumed to occur by surface diffusion, with the internal bulk remaining static. In a nano sized crystallite, surface and bulk energies can be comparable, and it is therefore not obvious that shape stability will depend on surface excitations alone. Moreover, surface facets can be extremely small. In our simulations (see our Fig. 1), the initial rod facets are only several atoms across. It is not apriori obvious that concepts such as roughening, defined for macroscopically large surfaces, will apply to surfaces so small. It is therefore important, and not obvious, that we find nanorod stability is nevertheless still governed by the stability of the exposed facets, and that the roughening of the facets does seem to serve as the mechanism for nucleating shape transformation. Once a facet roughens, however, the resulting shape transformation proceeds via a complete
rearrangement of the internal bulk atoms of the rod, a very different process from the surface diffusion expected for micro or larger sized crystals (hence the title of our work, which emphasizes this point).

The experimental paper by Spiller that referee A cites, is of relevance to our work and we were not aware of it. This work shows that Pb clusters of nanometer size (10-50nm) with large exposed {111} facets can be superheated above melting. This is in agreement with our finding that {111} facets can stabilize a Au nanorod. However this paper does not make any direct connections between shape stability and surface roughening. Indeed the conclusion of the paper is that the stability of such clusters is likely due to the difficulty of nucleating a liquid drop on the {111} surface; the authors argue that the stability is thus a kinetic effect, rather than an equilibrium effect such as roughening. This paper also does not mention anything about the effect of exposed {110} surfaces on shape stability below melting. Thus while this paper gives experimental support to some of our conclusions, it does not at all present the general connection between shape stability and surface roughening that is the focus of our simulations. The experimental paper by Grabeck et al. that referee A cites, concerns the superheating and supercooling of Pb crystallites embedded in an Al matrix. We did not see anything in this paper that measured this effect to be a consequence of large exposed {111} facets or any particular shape geometry.

In response to referee A’s comments, we have modified our first two paragraphs and our conclusion to make reference to the works of Metois and Spiller discussed above, and to further clarify the connection of the theory of equilibrium shapes to nano sized clusters.

Reply to referee C

In his first review, referee C described our work as an “original study” that “is very interesting”. He then raised several criticisms concerning our “interpretation of the results”. Foremost among these criticisms was, “From my point of view, I don’t understand the necessity to introduce the roughening transition. Why could the observed results not simply be explained by a change in the most stable facet as a function of temperature?” Of course, for macroscopically large surfaces, roughening is exactly what determines the stability of a facet as temperature varies (see our Ref. [2]). This point, that referee A considers so obvious as to make our results uninteresting, is the point over which referee C ultimately rejects our paper as he does not believe in it.

In our first reply, we attempted to address in detail all of C’s comments. In referee C’s second review, he raises only the single objection concerning our interpretation of the shape instability as due to the roughening of the {110} facets. Unlike referee A, we did not regard this interpretation as obvious, due to the nano size of our cluster as we have discussed above. Rather we tried to reply to referee C in as detailed way as possible. As part of our response we decided to rephrase our paper to refer to the {110} surface “instability”, rather than the {110} surface “roughening”, throughout most of the paper. We did this because we could not claim our proof of the connection to roughening was
truly definitive. However, since we felt the connection was natural (referee A thinks it is obvious) and our data supported this, we suggested this connection in our 4th paragraph from the end. This revision was unsatisfactory to referee C. He does not believe roughening is involved, and demands that we either agree with him or give a “rigorous explanation” that the connection to roughening is correct.

Following up on a comment in our first reply to him, referee C says that “a finite size transition temperature could be locate by a peak or a kink in a thermodynamic quantity or correlation function: may I suggest the authors to calculate such quantities to definitely show their claims”. We made this statement about locating a finite size transition temperature in connection with previous theoretical calculations of specific heat $C_v$ in an SOS model for surface roughening (Kohanoff, Jug and Tosatti, J. Phys. A 23, L209 (1990)). For simulations of a real cluster (unlike an SOS model) such as we have done, excitations of the bulk naturally coexist with excitations of the surface, and one cannot separate out the contribution to $C_v$ due to surface fluctuations as distinct from bulk fluctuations. Since the roughening transition is generally expected to be in the Kosterlitz-Thouless universality class, and so $C_v$ has only a mild finite cusp above the transition (further rounded out by finite size effects), rather than a divergence at the transition, and since the contribution to $C_v$ from bulk excitations is at least as big if not bigger than that from the surface, our simulations do not have the precision to see such a feature. Moreover, even if we had found such a feature in $C_v$, there would be nothing to prove that it was specifically associated with roughening, rather than some other instability. We therefore took instead the approach of determining roughening via the direct connection between roughening and faceting as detailed in our Ref.[2] (and earlier mean field theories of equilibrium shape). In Fig. 4 we compute the average rod profile looking down the long axis, and identify the vanishing of the initial flat $\{110\}$ facets as being at approximately the same temperature ~400 K where measurement of the radius of gyration in Fig. 2 indicates the start of the shape transformation. The small size of our system, and the discreteness of atoms on the surface, limit the accuracy with which we can determine a precise transition temperature with this method. Hence we feel our connection between shape instability and roughening cannot be said to be definitive. However it is certainly consistent enough to justify our suggesting this as the probable mechanism. We have explained these points in our first reply to referee C (our point (2)), however he has entirely ignored our remarks about this in his second review.

To conclude, we have carried out what we believe are the first systematic calculations of shape instability in nanorods using a realistic interaction for Au atoms. We show that shape stability is related to the stability of the particular low index surface facets. For nano size clusters, where surface and bulk free energies are comparable, we believe that these results do not trivially follow from the usual theory of equilibrium shapes. When the rod $\{110\}$ facets become unstable, and nucleates the shape instability, the shape transformation proceeds via a reorganization of the bulk atoms, rather than by surface diffusion. This is contrary to the usual picture from the theory of equilibrium shapes. We have tried to relate our observed surface instabilities to the roughening transition of the corresponding macroscopic low index surface. Despite the very small size of our facets, we find our results clearly suggest this interpretation. We feel that our specific
simulations, together with the more general interpretation they provide, are new and interesting, and will help clarify what (judging by the conflicting reviews of referees A and C) is still a topic of confusion.