String Tension and Stability of Magic Tip-Suspended Nanowires

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Interest in the physical properties of nanosized metal contacts and tip-suspended nanowires, previously restricted mostly to quantized ballistic conductance, is currently rising. Recent breakthrough Transmission Electron Microscope (TEM) images have provided unprecedented detail about the structure and evolution of necks, bridges and wires formed between gold tips. [2, 3, 4, 5]. They showed among other things that (110) gold nanobridges, which possess a regular crystalline fcc structure when sufficiently thick or short, can develop after thinning below a diameter of roughly 15 Å into very regular but now noncrystalline nanowires hanging between tips several nanometer apart. Remarkably, the new nanowires come mostly in discrete, magic structures (Fig.1), described as coaxial shells or tubes, each tube roughly a triangular sheet folded cylindrically onto itself [4], as in a carbon nanotube.

The reasons why that can be exciting are manifold. Wires in general represent a novel organization of matter – similar but not identical to clusters – which is yet to be fully understood. [6] A structural transition from crystalline (fcc) to noncrystalline nanowires including chiral ones was predicted theoretically for decreasing radius [7]. Non-equilibrium necks and their nanosecond evolution have been relatively well explored particularly through simulation, but these long-lived magic nanowires (the time scale is seconds at room temperature) are not particularly within the simulation reach. More generally the connection between thermodynamical, geometrical, mechanical, electronic properties in these nanowires calls for a fresh approach.

In our theory work [8] we showed first of all that wire-tip grand canonical equilibrium is described not just by the total wire free energy, but by its string tension, measuring the force between the two tips. That represents an important step, because it allows the description of quasi-equilibrium of a nanowire segment suspended between two tips, and slowly exchanging atoms with them, to be done based on information about an infinite regular nanowire and an infinite regular bulk – both objects much simpler than the real one. Among other things, the quasi-equilibrium string tension being the force pulling the tips together, it can and has been measured.

Tension drives the nanowire evolution, and a generally positive tension implies that a nanowire will shrink by gradually losing atoms to the tips in the course of time. [9] That leads to a decrease of tension, which falls to zero as the nanowire eventually breaks. Before that happens, the thinning evolution will occasionally take a nanowire through a few perfect, smooth structures, whose added stability will reflect in a local minimum of the string tension. Our proposal was therefore that the observed magic nanowires should coincide with local minima of the string tension, as that is a state where the nanowire diameter will (for a while) neither grow nor drop.

After a systematic classification of possible coaxial tube wires, similar in spirit to that of carbon nanotubes, the theory work is in principle feasible by explicit calculations of string tension. We demonstrated that this can be readily achieved, through state-of-the-art density functional electronic structure calculations, which we carried out for the simplest and thinnest coaxial gold and silver nanowires of various diameters and chiralities, all with optimized structure.

We found (Fig. 2) a clear string tension minimum for a single-tube [(7,3)-1] gold nanowire which is chiral and consists of seven strands – in striking agreement with observation.

Furthermore we were able to characterize the electronic structure of several wires (Fig. 3) showing that, for Au, the magic structures are not connected with electron shell closing. The number of bands crossing the Fermi level, which we also provided, gave information on the ballistic conductance of these wires which remains to be investigated experimentally.

Finally, with theory and experiment in agreement for the geometrical structure, the microscopic physics remained to be understood. Why seven strands and not six, or five? Why is a chiral nanowire best, and why with just that (7,3) chirality? Here what helped was a direct comparison of gold with silver, another noble metal which is indeed very similar to gold, but that does not possess the so-called surface reconstructions typical of gold.

Calculations showed that the seven strand [(7,3)-1] nanowire should be no longer strongly stabilized in silver. Nanowires possessing a less crowded surface structure are likely to be stabilized, as is also the case with all ordinary crystal surfaces of silver.

In conclusion, the view that the shape of noble metal nanowires, like that of nanoclusters, is dominated by optimization of their surface [7] appears to be theoretically established.

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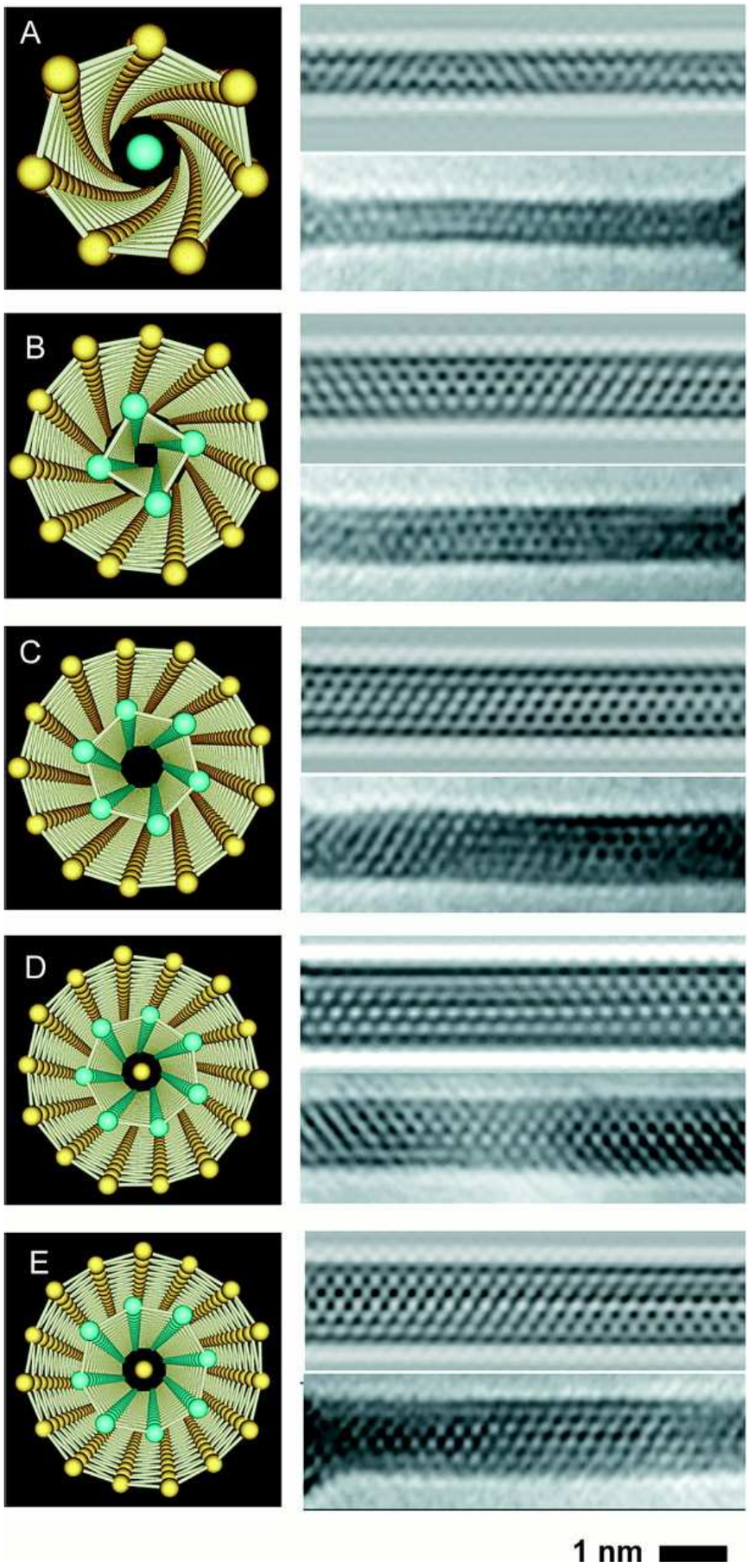
1 Figure Captions

Figure 1. Experimental multi-shell structure of gold nanowires. The left part of the figure shows model axial views. The right part shows the experimental TEM images (lower) and the simulated immages (upper). Taken from Ref.[4].

Figure 2. Calculated string tension of several tip-suspended gold nanowires. The minimum demonstrates why (7,3) is magic.

Figure 3. Electronic structure of selected gold nanowires. Full (empty) dots mark single (doubly degenerate) Fermi crossings, indicating 6,6, and 8 conducting channels respectively. Upper inset in (7,3) panel is a magnified detail of the bands crossing the Fermi level (the vertical scale is from -0.5 to 0.125 eV).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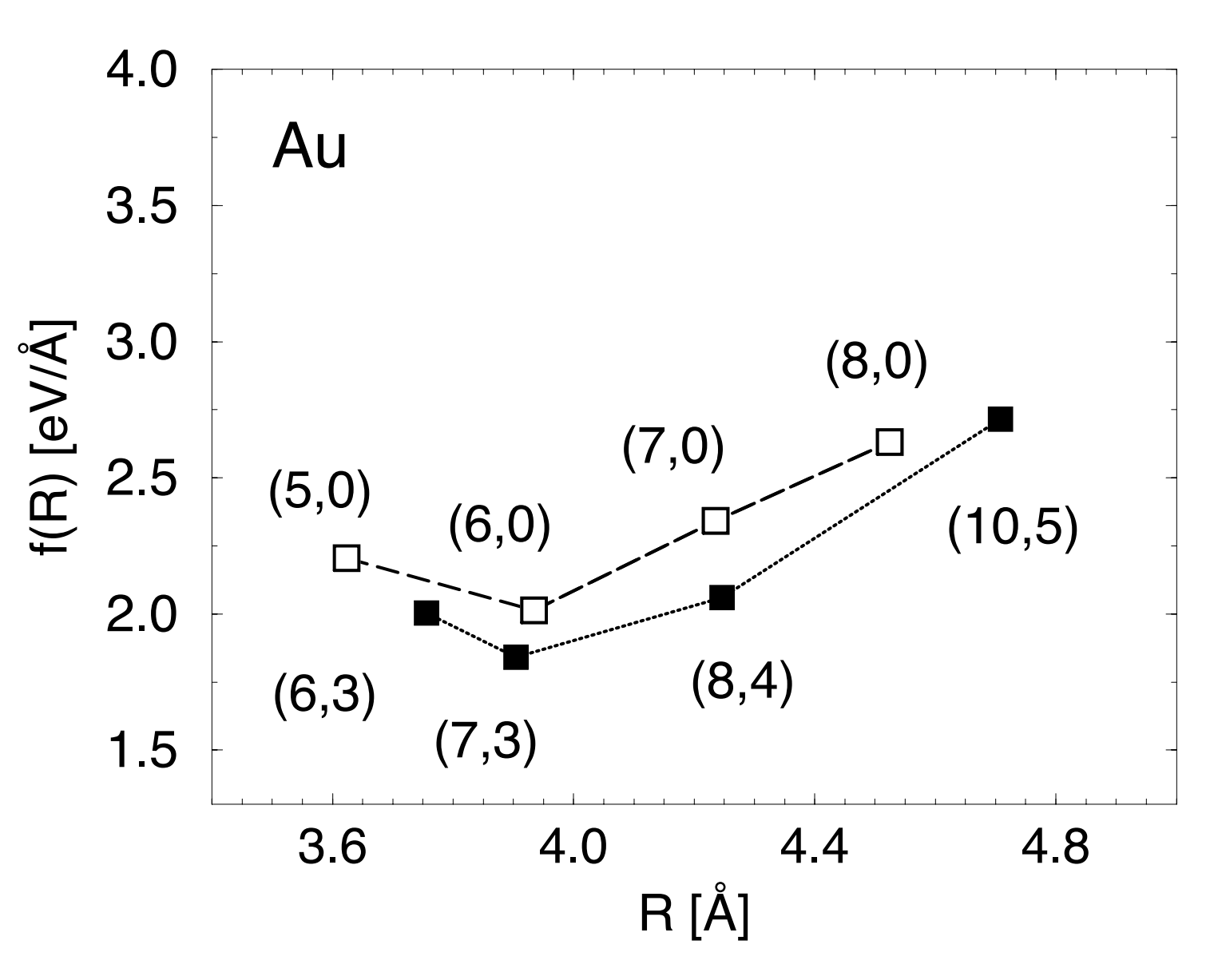
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R [Å]
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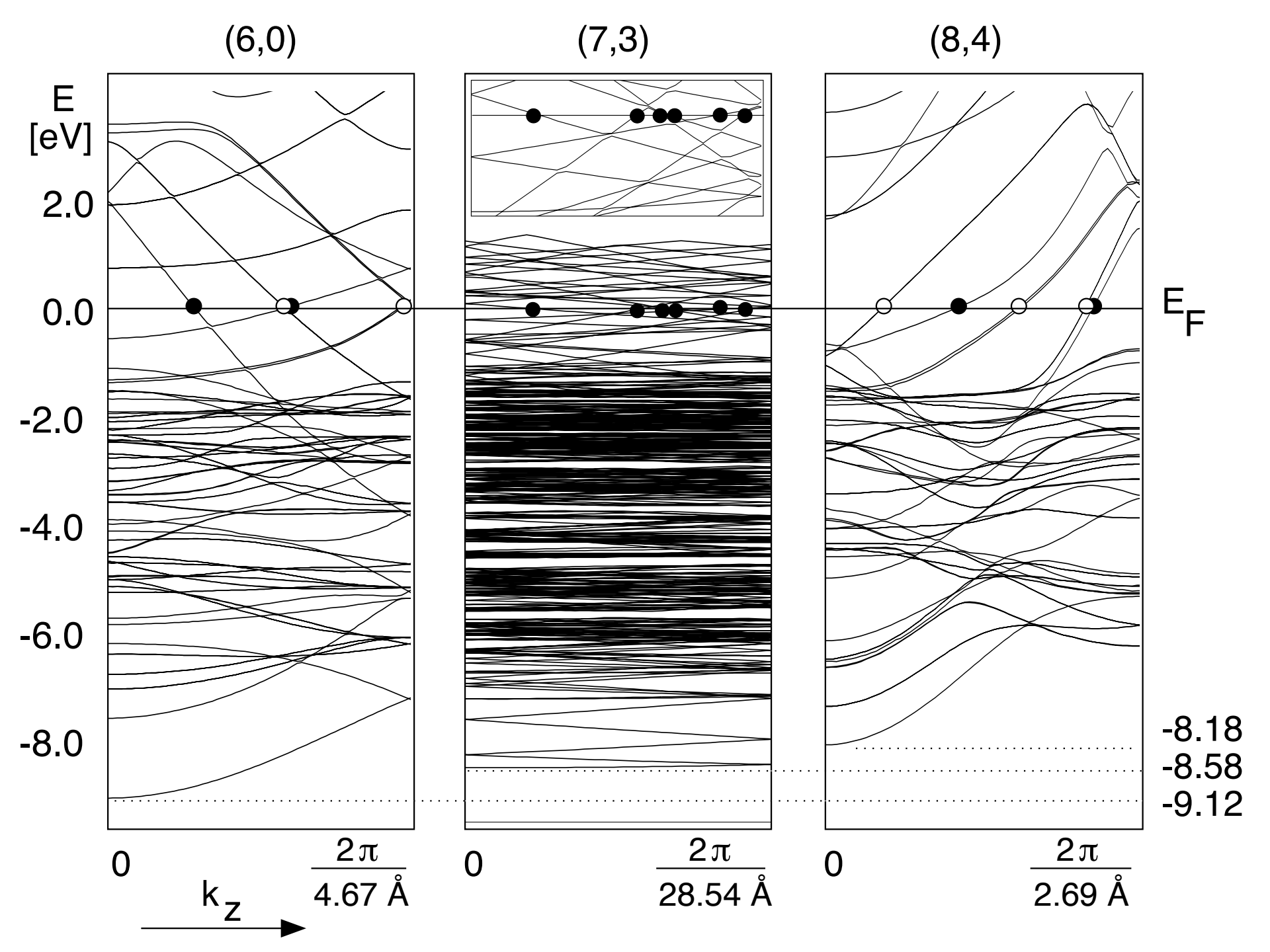
3.0
2.5
2.0
1.5
3.6
4.0
4.4
4.8
(5,0)
(6,0)
(7,0)
(8,0)
(10,5)
(6,3)
(7,3)
(8,4)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(7,3)
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-8.58
-9.12
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0
2π
28.54 Å
0
2π
2.69 Å
k_z