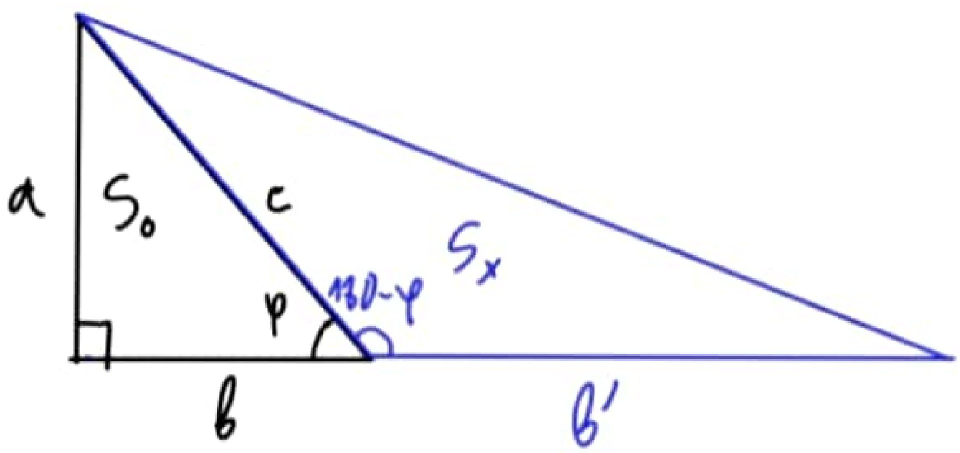
I want to geometrically prove that $\cos(\pi - \phi) = -\cos\phi$ without resorting to the unit circle or trigonometric formulas, but have difficulties figuring it out.

It's easy enough to do the sine, however: you draw a right triangle to complement the existing scalene triangle and then subtract the area of the smaller right triangle from the bigger one (see picture).



$$a = c\sin\phi$$

$$S_x = \frac{c\cdot\sin\phi\cdot(b+b')}{2} - \frac{c\cdot\sin\phi\cdot b}{2}$$
$$= \frac{c\cdot\sin\phi\cdot b'}{2}$$

On the other hand,

$$S_x = \frac{c\cdot\sin(\pi-\phi)\cdot b'}{2}$$

Thus,

$$\sin(\pi-\phi) = \sin\phi$$

I'll be grateful for any ideas/advice.

Thanks to @Blue for the idea; also, please check out the post referenced in the question's comments, since there may be a fundamental flaw in this approach to reasoning altogether.

Still, let us build an isosceles scalene triangle ($c = b'$). In that case, the longer hypotenuse can be calculated twofold:

$$(b + b')^2 + (b' sin\phi)^2 = 2b'^2 - 2b'^2 cos(\pi - \phi)$$

Knowing that $b = b' cos\phi$,

$$b^2 + 2bb' + b'^2 + b'^2 sin^2\phi = 2b'^2 - 2b'^2 cos(\pi - \phi)$$

$$b'^2 cos^2\phi + b'^2 sin^2\phi + 2b'^2 cos\phi = b'^2 - 2b'^2 cos(\pi - \phi)$$

$$cos\phi = -cos(\pi - \phi)$$