cos^{-1} is a function such that $cos^{-1}(t)$ is an angle x from $[0; 2\pi)$ such that $cos(x) = t$.

We know that $cos(\pi/3) = 1/2$. Also from trigonometry $cos(\pi - y) = -cos(y)$ for every real y.

Then

$cos(\pi/3) = 1/2 = -cos(\pi - \pi/3) = -cos(2\pi/3)$

$cos(2\pi/3) = -1/2$

Now we get for angle $2\pi/3$ equality $cos(2\pi/3) = -1/2$. Then by definition $cos^{-1}(-1/2) = 2\pi/3$