

Supporting Information

for

Mechanical deformation affects the counterions condensation in highly-swollen polyelectrolyte hydrogels

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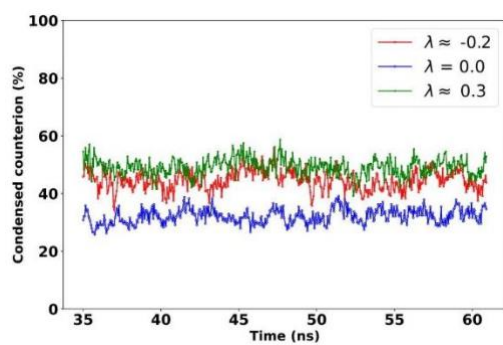
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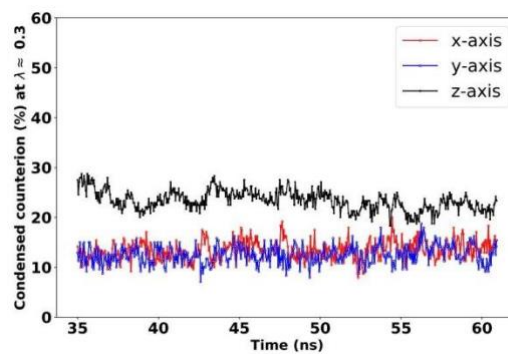
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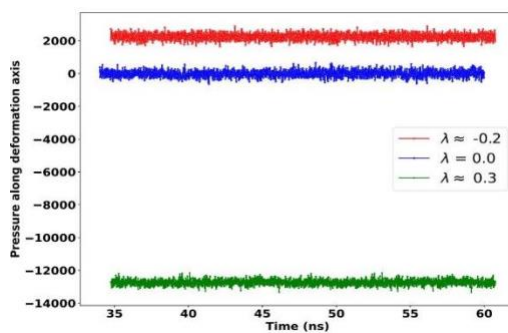
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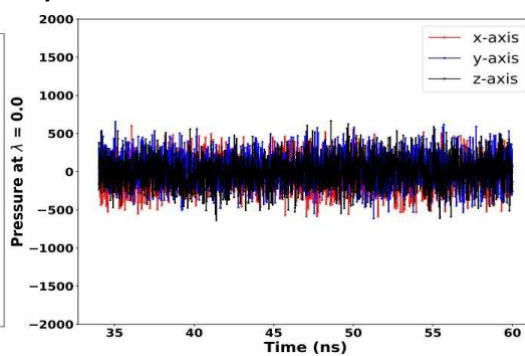
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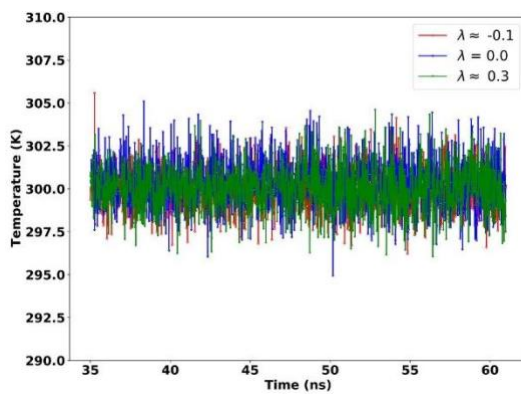
c)



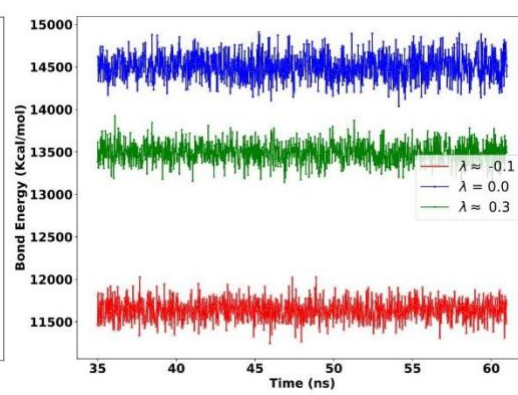
d)



e)



f)



g)

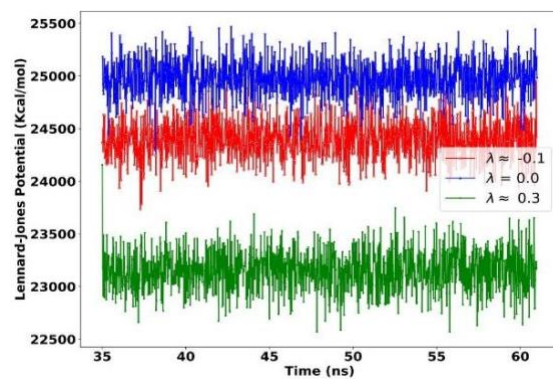
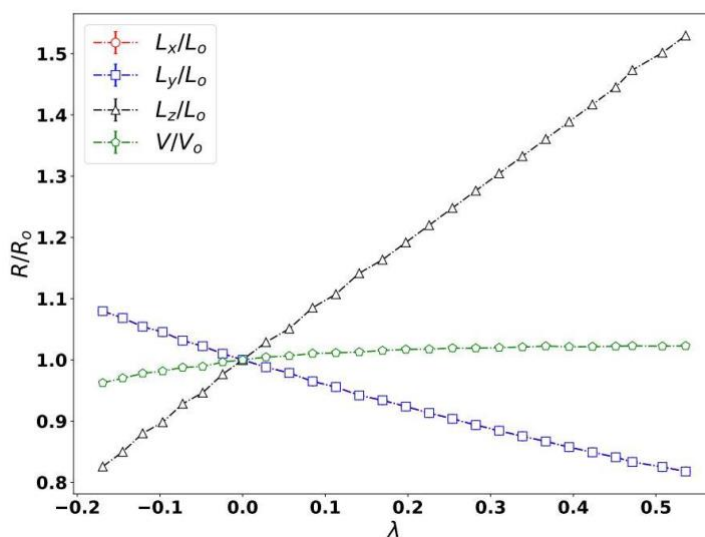


Figure S1. a) Total condensation of counterions for three different deformation ratios, λ : b) the amount of condensed counterion around the chains aligned in all three directions at $\lambda \approx 0.3$, c) the pressure along the deformation (\hat{z} – *axis*) direction for various λ cases, d) the pressure at $\lambda = 0.0$. e) Temperature is maintained at $T = 300\text{ K}$, f) bonded and g) non-bonded (non-electrostatic energies) as a function of simulation time.

a)



b)

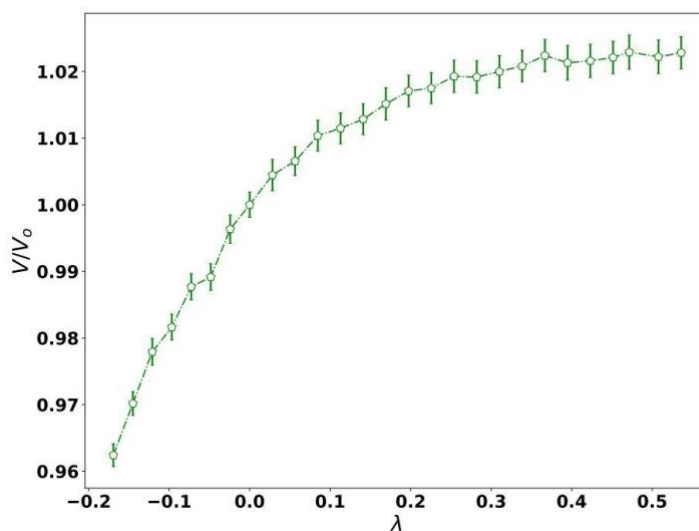


Figure S2: Changes in the simulation box dimensions and the total hydrogel volume. Note that in each direction there are two crosslinks such that the end-to-end distance of chains between two crosslinks is $L_i/2$, where $i=x,y,z$.

a)

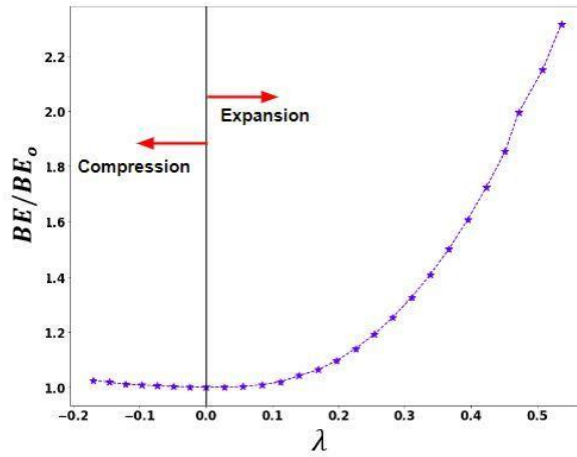
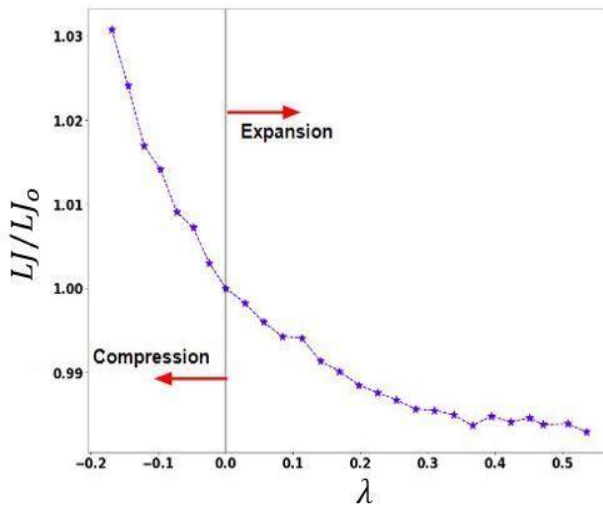
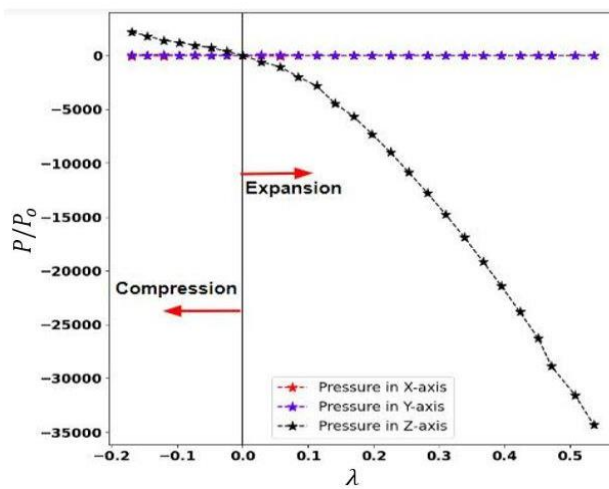


Figure S3: a) Increase in the bond energy
b) Lennard-Jones potential as the hydrogel is stretched. In the deformed states, the pressure in the undeformed (x – axis and y – axis) remains constant, and the pressure in the deformation axis (z – axis) changes. All the values are normalized by the value at $\lambda = 0$.

b)



c)



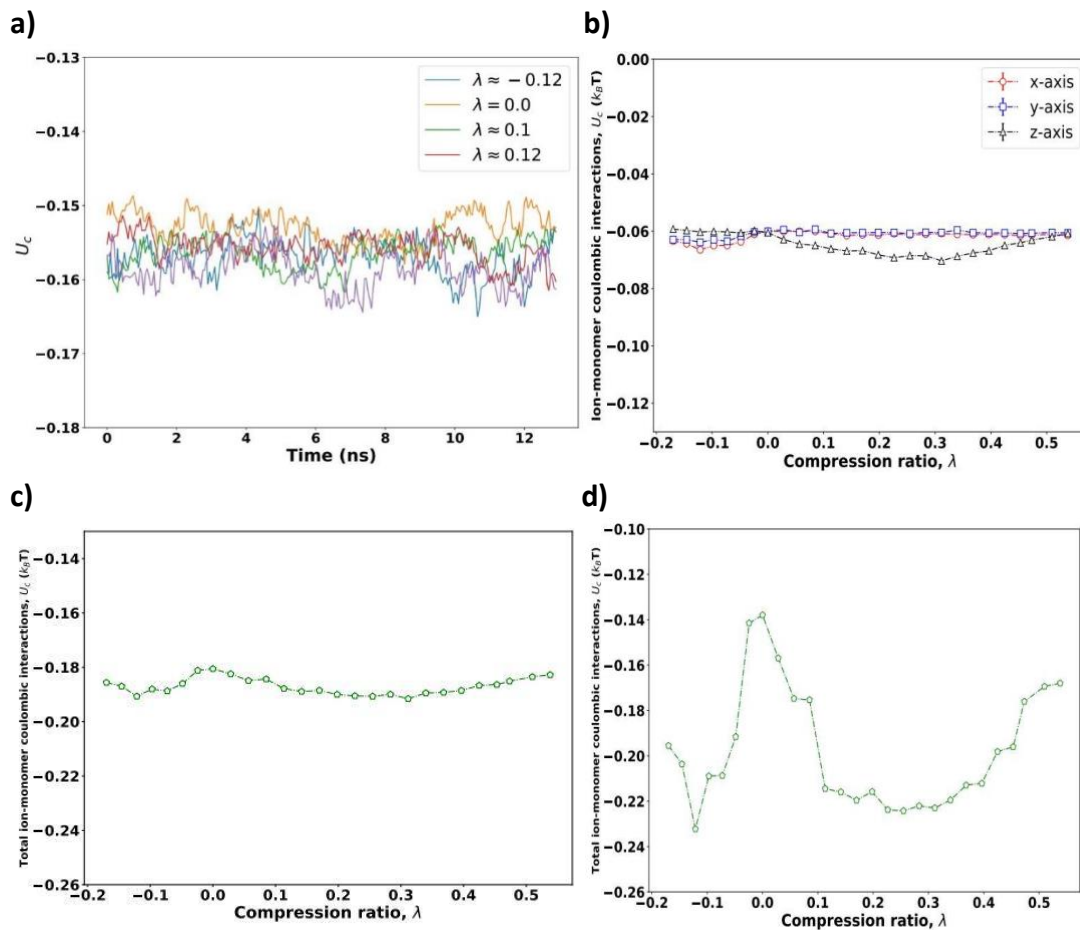


Figure S4. Coulomb interactions between negative charge on monomers of hydrogel and sodium counterions are computed at the cut-off distance, $r_c = 1.5 \text{ nm}$. a) The total Coulomb energy change during last 13 ns of simulations for different deformations cases are shown b) The change in the Coulomb energy along the three different axis as the hydrogel is deformed at $r_c = 1.5 \text{ nm}$ c) The total Coulombic interactions as a function of strain, d) Sort-range pairwise Coulomb interactions per ion at $d < 0.25 \text{ nm}$.

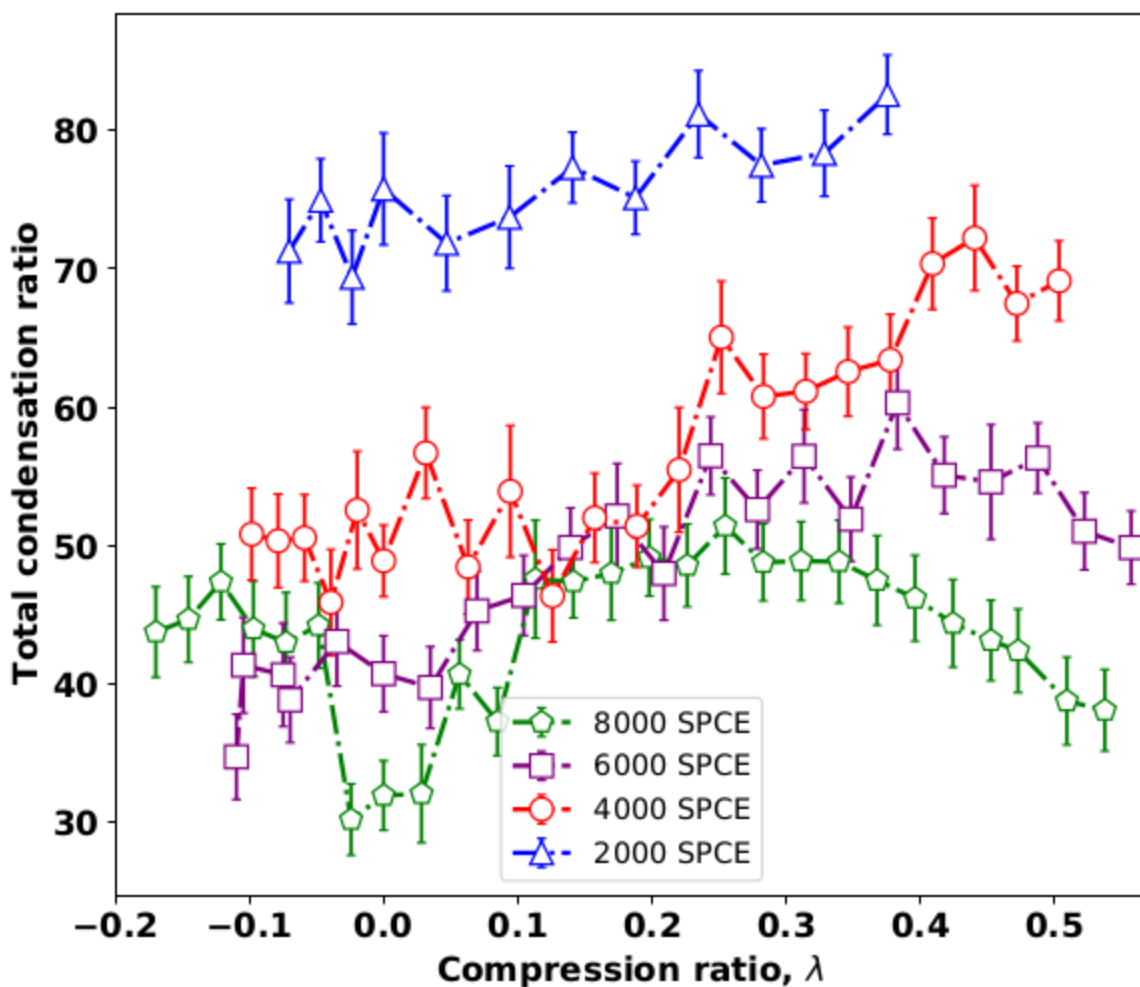
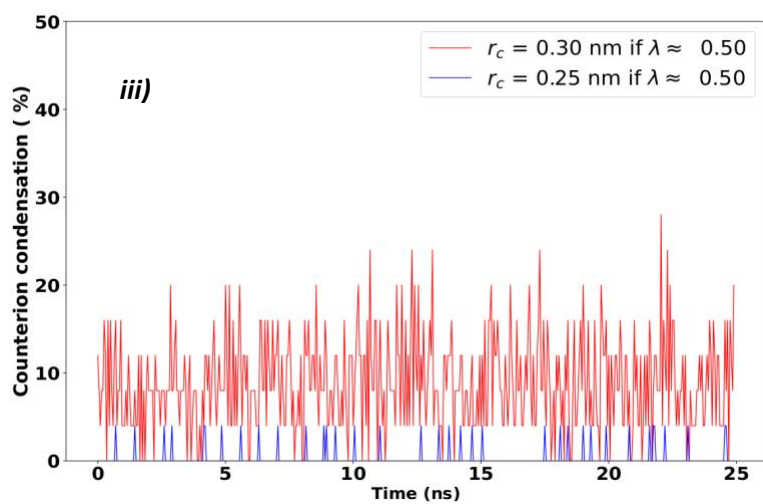
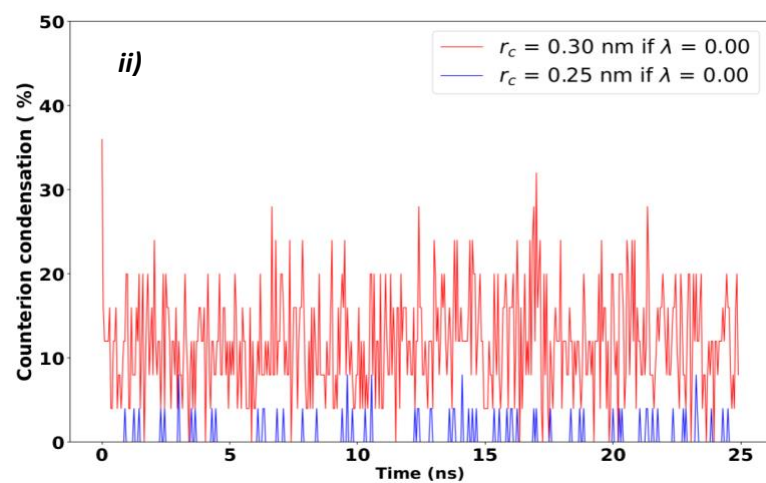
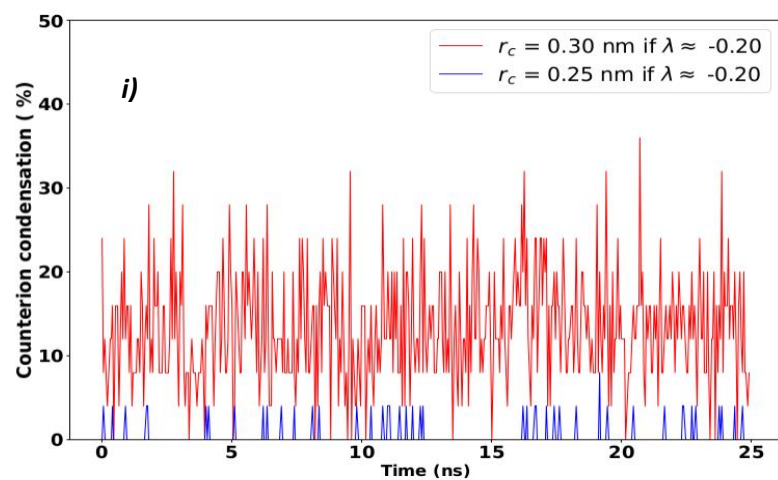


Figure S5. This figure shows a total counterion condensation for a different number of SPC/E molecules. All cases show an increase in total condensation with respect to deformation. However, for highly and intermediately swollen cases (8000, 6000 and 4000 SPC/E), approximately 20 % increase in the total condensation is observed from their respective NPT ensemble states. Whereas, for less swollen case (2000 SPC/E) only 5 to 10 % change in total condensation is observed.

a)



b)

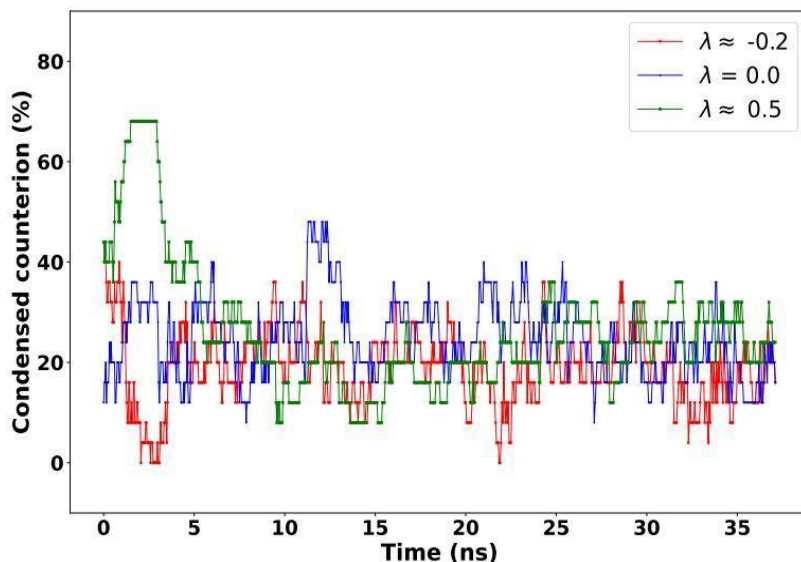


Figure S6. This figure represents the time evolution of condensation of counterions for implicit and explicit solvent. a) Implicit solvent case; time evolution of condensation of counterions using two different cut-off distances (0.25 and 0.3 nm) for *i)* maximum compression ($\lambda = -0.2$), *ii)* NPT ensemble ($\lambda = 0.0$), *iii)* maximum stretching ($\lambda = 0.5$). It is clear in all cases that for cut-off 0.25 nm, we observe very few condensed counterions as compared to 0.3 nm cut-off distance case. b) Explicit solvent case; time evolution of condensation of counterions is shown for $\lambda = -0.2, 0.0$,and 0.5 cases.