Chapter 3

Chemo-mechanical Modeling-I

3.1 Analytical expression of stresses-elastic deformation

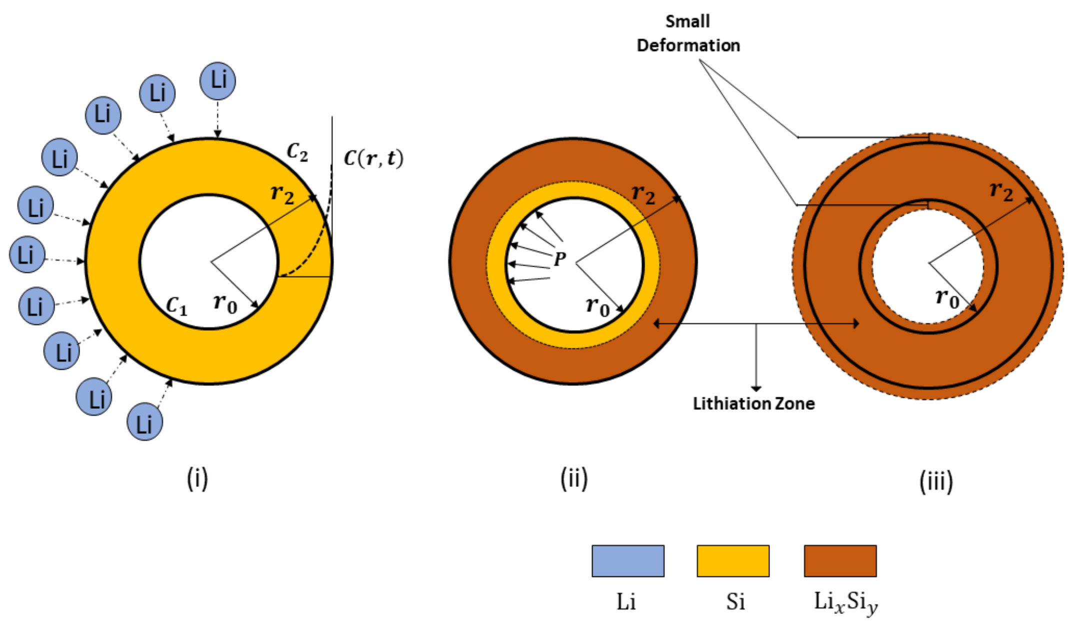


Figure 3.1: (i) Lithium diffusing into the silicon hollow particle, (ii) Lithium and silicon forms an alloy at the interface (lithiation Zone), (iii) Diffusion and electrochemical reaction of lithium with silicon leads to the volumetric expansion

Modeling and analytical solutions for the hollow silicon sphere intercalating with Lithium for infinitesimally small deformation under the elastic and plastic region at inner and outer surfaces are presented in this context. A hollow silicon sphere initially undeformed has inner and outer radius as r_0 and r_2, respectively, as shown in Fig-(3.1). Through spherically symmetric deformation around the hollow spherical particle, the spherical polar coordinate (r, θ, ϕ)

denotes the particle location in the deformed configurations. C_2 and C_1 signifies the Lithium concentration at the hollow silicon sphere's outer and inner surface, respectively. P is the applied compressive stress (internal pressure) at the inner wall of the hollow silicon sphere.

3.1.1 Reaction induced stress (RIS)

Considering electrochemical reaction during the insertion of Lithium in the electrode, where Lithium acts as the solute atoms and Silicon as the host, and Li_xSi_y is the reaction product of the forward reaction between Lithium and Silicon.

$$\mathrm{Li}^+ + \mathrm{e}^- \longrightarrow \mathrm{Li}(\text{at the electrode/electrolyte interface})$$

$$\mathrm{xLi} + \mathrm{ySi} \longrightarrow \mathrm{Li}_x\mathrm{Si}_y(\text{at the electrode})$$

Where reaction strain caused by the above electrochemical reaction (First order reaction) is proportional to the difference of atomic volume between reactants and the reaction product [31]. The volumetric expansion of a particle during the intercalation is caused by both diffusion as well as electrochemical reaction (forward as well as backward), creating pressure and tension during lithiation and delithtation of solute atoms (lithium) [32] [33]. The backward reaction can be ignored for the potentiostatic study [34]. Eq-(3.1) shows the volumetric strain causes by the forward reaction.

$$\varepsilon_{reaction} = \bar{V} S_f \tag{3.1}$$

Where, $\bar{V}$ is the difference between the reaction product atomic volume and the reactant product atomic volume, and S_f is the portion of forward reaction product. Based on the law of mass action [35] we can define S_f as,

$$S_f = \alpha \int_0^t r_f \; dt' \tag{3.2}$$

Where, α is the proportionality constant, r_f is the rate of forward reaction between Lithium and Silicon which is further defined as $r_f = kC\left(r, t\right)$, Whereas k is the rate constant of forward reaction and $C(r,t)$ is the concentration function.

$$S_f = \alpha \int_0^t kC(r,t')\,dt' \tag{3.3}$$

The general expression of $C(r,t)$ (concentration function-Appendix-A) for the hollow spherical particle [36] is given below. C_2 is the concentration of lithium atoms at the outer surface of the hollow silicon particle , whereas C_1 is the concentration of lithium atoms at the inner surface of the hollow silicon particle and $f(r)$ is the initial concentration function. Where as $\tau = \dfrac{Dt}{(r_2 - r_0)^2}$,

$$\begin{aligned} C(r,t) &= \frac{r_0 C_1}{r} + \frac{(r_2 C_2 - r_0 C_1).(r - r_0)}{r(r_2 - r_0)} \\ &+ \frac{2}{r\pi}\sum_{n=1}^{\infty}\left(\frac{r_2 C_2 cos n\pi - r_0 C_1}{n}\right).exp\left(-n^2\pi^2\tau\right).sin\left(n\pi\left(\frac{r - r_0}{r_2 - r_0}\right)\right) \\ &+ \frac{2}{r(r_2 - r_0)}\sum_{n=1}^{\infty} exp\left(-n^2\pi^2\tau\right).sin\left(n\pi\left(\frac{r - r_0}{r_2 - r_0}\right)\right)\int_{r_0}^{r_2} r' f(r').sin\left(n\pi\left(\frac{r' - r_0}{r_2 - r_0}\right)\right)dr' \end{aligned} \tag{3.4}$$

Eq-(3.5) is the special case of the general expression of the concentration function Eq-(3.4) representing diffusion of lithium atoms from outer to inner surface of the hollow silicon particle (lithiation)

$$C(r,t) = \frac{r_2(r - r_0)C_2}{r(r_2 - r_0)} + \frac{2r_2C_2}{r\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}.exp\left(-n^2\pi^2\tau\right).sin\left(n\pi\left(\frac{r - r_0}{r_2 - r_0}\right)\right) \tag{3.5}$$

Similarly, Eq-(3.6) is the other special case for the general expression of the concentration function representing diffusion of lithium atoms from inner to outer surface of the hollow silicon particle (Delithiation).

$$C(r,t) = \frac{r_0C_1}{r} - \frac{r_0(r - r_0)C_1}{r(r_2 - r_0)} - \frac{2r_0C_1}{r\pi}\sum_{n=1}^{\infty}\frac{1}{n}.exp\left(-n^2\pi^2\tau\right).sin\left(n\pi\left(\frac{r - r_0}{r_2 - r_0}\right)\right) \tag{3.6}$$

From Eq-(3.3), we get,

$$S_f = k\alpha \int_0^t C(r, t')\, dt' \tag{3.7}$$

Substituting above expression in Eq-(3.1), we get the expression for the volumetric strain caused by reaction induced stress as

$$\varepsilon_{reaction} = \bar{V} k\alpha \int_0^t C(r, t')\, dt' \tag{3.8}$$

Dividing and multiplying the above expression with Ω (partial molar volume of lithium) we get,

$$\varepsilon_{reaction} = \frac{\bar{V} k\alpha}{\Omega} \Omega \int_0^t C(r, t') dt' \tag{3.9}$$

Whereas the ξ can be expressed as,

$$\xi = \frac{\bar{V} k\alpha}{\Omega} \tag{3.10}$$

Considering the range of ξ between 0 to 1 during the analysis [32] [34]. Rearranging Eq-(1.9), we get,

$$\varepsilon_{reaction} = \xi\Omega \int_0^t C(r, t')\, dt' \tag{3.11}$$

The approximate expression of stress (Reaction induced stress) generated due to above formation of Li_xSi_y alloy is given by,

$$\sigma_{approx}(r, t) = -\frac{E}{3(1-2\nu)} \varepsilon_{reaction} \tag{3.12}$$

The strain caused by the diffusion induced stress (DIS) is given by $\varepsilon_{diffusion} = \Omega C(r, t)$, whereas the strain caused by the reaction induced stress (RIS) is given by Eq-(3.11). Therefore, the total strain caused by both the stresses is given by,

$$\varepsilon_t = \Omega C\left(r,t\right) + \xi\Omega \int_0^t C\left(r,t'\right)dt' \tag{3.13}$$

Substituting Eq-(3.11) in Eq-(3.12) we get the approximate model for Reaction induced stress (RIS),

$$\sigma_{approx}\left(r,t\right) = -\frac{E\xi\Omega}{3\left(1-2\nu\right)} \int_0^t C\left(r,t'\right)dt' \tag{3.14}$$

The above expression is the approximate stress induced by the electrochemical reaction between lithium and silicon [32] to the overall stresses,

3.1.2 The generalized expression of radial displacement function corresponding to diffusion and reaction induced stress

The spherical coordinate system (r, θ, ϕ) is used to define the spherical electrode. The material element is subjected to a state of tri-axial stresses (σ_r, σ_θ, σ_ϕ) where σ_r is the radial stress and σ_θ (Normal component in θ direction) is the hoop stress considering $\sigma_\theta = \sigma_\phi$ (Normal component in ϕ direction) to be assumed implicitly. The stress is the function of radius and time (in homogeneous); therefore, the partial differentiation of the function gives rise to the relation of balance of forces acting on the material elements [37] which also implies the characteristic time for the elastic deformation of the spherical electrode being smaller than that for the migration of solute atoms (Lithium in this case) [38]. Mechanical equilibrium is therefore treated as subject for static equilibrium equations in the absence of body reduces to

$$\frac{\partial\sigma_r\left(r,t\right)}{\partial r} + 2\frac{\sigma_r\left(r,t\right) - \sigma_\theta\left(r,t\right)}{r} = 0 \tag{3.15}$$

Further we can define radial and hoop strain for the above representation as,

$$\varepsilon_r = \frac{\partial u_r\left(r\right)}{\partial r},\ \varepsilon_\theta = \frac{u_r\left(r\right)}{r} \tag{3.16}$$

where $u_r(r)$ is the radial displacement function.The material is assumed to be homogeneous, isotropic, linear-elastic solid and the material properties including Young's modulus E, Poisson's ratio v, and the partial molar volume Ω, whereas parameter ξ corresponding to the relative rate of reaction and diffusion . The diffusion of lithium or into the Silicon can introduce local volumetric expansion and mechanical stress [39], therefore stress corresponding to diffusion and electrochemical reaction with host atoms can be considered together as stated in Eq-(3.13). Putting ξ=0 states only the diffusion of lithium into the host atoms without taking part in any of the reaction or formation of alloy. Eq-(3.17) and Eq-(3.19) represents the strain components (elongation in radial and hoop (tangential) direction.

$$\varepsilon_r = \frac{1}{E}\left(\sigma_r - 2\nu\sigma_\theta\right) + \frac{1}{3}\varepsilon_t \tag{3.17}$$

Substituting Eq-(3.13) in Eq-(3.17), we get,

$$\varepsilon_r = \frac{1}{E}\left(\sigma_r - 2\nu\sigma_\theta\right) + \frac{1}{3}\left(\Omega C\left(r,t\right) + \xi\Omega\int_0^t C(r,t')dt'\right) \tag{3.18}$$

Similarly,

$$\varepsilon_\theta = \frac{1}{E}\left(\left(1-\nu\right)\sigma_\theta - \nu\sigma_r\right) + \frac{1}{3}\varepsilon_t \tag{3.19}$$

Substituting Eq-(3.1) in Eq-(3.19), we get,

$$\varepsilon_\theta = \frac{1}{E}\left(\left(1-\nu\right)\sigma_\theta - \nu\sigma_r\right) + \frac{1}{3}\left(\Omega C\left(r,t\right) + \xi\Omega\int_0^t C\left(r,t'\right)dt'\right) \tag{3.20}$$

Reordering above expressions in order to evaluate the expression for σ_r and σ_θ, we get

$$\sigma_r\left(r,t\right) = \frac{E}{\left(1+v\right)\left(1-2v\right)}\left(\varepsilon_r\left(1-v\right) + \ 2v\varepsilon_\theta - \frac{\left(1+v\right)}{3}\left(\Omega C\left(r,t\right) + \ \xi\Omega\int_0^t C\left(r,t'\right)dt'\right)\right) \tag{3.21}$$

$$\sigma_\theta(r,t) = \frac{E}{(1+v)(1-2v)}\left(v\varepsilon_r + \varepsilon_\theta - \frac{(1+v)}{3}\left(\Omega C(r,t) + \xi\Omega\int_0^t C(r,t')\,dt'\right)\right) \tag{3.22}$$

Substituting Eq-(3.21) & Eq-(3.22) in Eq-(3.15) we get,

$$\frac{\partial}{\partial r}\left\{\left(\frac{\partial u_r(r)}{\partial r}(1-v) + 2v\frac{u_r(r)}{r} - \frac{(1+v)}{3}\left(\Omega C(r,t) + \xi\Omega\int_0^t C(r,t')\,dt'\right)\right)\right\}$$
$$+\frac{2}{r}\left\{\frac{\partial u_r(r)}{\partial r}(1-2v) - \frac{u_r(r)}{r}(1-2v)\right\} = 0 \tag{3.23}$$

Differentiating the above expression and substituting in Eq-(3.16),we get,

$$\frac{\partial^2 u_r(r)}{\partial r^2}(1-v) + \frac{2}{r}\frac{\partial u_r(r)}{\partial r}(1-v) - \frac{2u_r(r)}{r^2}(1-v)$$
$$= (1+v)\frac{\Omega}{3}\frac{\partial C(r,t)}{\partial r} + (1+v)\frac{\xi\Omega}{3}\int_0^t \frac{\partial C(r,t')}{\partial r}dt' \tag{3.24}$$

Rearranging the above expression, we get the expression for radial displacement function $u_r(r)$ as,

$$u_r(r) = \frac{(1+v)}{(1-v)}\frac{\Omega}{3r^2}\int_{r_0}^{r} r'^2 C(r',t)\,dr' + \frac{(1+v)}{(1-v)}\frac{\xi\Omega}{3r^2}\int_{r_0}^{r} r'^2\left(\int_0^t C(r',t')\,dt'\right)dr' + \frac{Ar}{3} + \frac{B}{r^2} \tag{3.25}$$

where $u_\theta = u_\phi = 0$ [40], also θ and ϕ having high degree of symmetry (simplified geometric relations) [41]. The expression for the radial displacement function obtained above considering ξ=0 is similar to expression obtained by the work of Feng Hao et.al [42], where r_0 is the convenient lower limit for the integral-inner radius of the hollow sphere, whereas in case of solid sphere r_0 is equal to zero as stated by Yong Li et.al [38]. Substituting Eq-(3.25) in Eq-(3.16) corresponding to radial strain, we get,

$$\varepsilon_r = -\frac{2(1+v)}{3(1-v)}\frac{\Omega}{r^3}\int_{r_0}^{r} r'^2 C(r',t)\,dr' - \frac{2(1+v)}{3(1-v)}\frac{\xi\Omega}{r^3}\int_{r_0}^{r} r'^2\left(\int_0^t C(r',t')\,dt'\right)dr'$$
$$+\frac{A}{3} - \frac{2B}{r^3} + \frac{(1+v)}{(1-v)}\frac{\Omega C(r,t)}{3} + \frac{(1+v)}{(1-v)}\frac{\xi\Omega}{3}\int_0^t C(r,t')\,dt' \tag{3.26}$$

Similarly, Substituting Eq-(3.25)in Eq-(3.16) corresponding to hoop strain, we get,

$$\varepsilon_\theta = \frac{(1+v)}{3(1-v)}\frac{\Omega}{r^3}\int_{r_0}^{r} r'^2 C(r',t)\,dr' + \frac{(1+v)}{3(1-v)}\frac{\xi\Omega}{r^3}\int_{r_0}^{r} \acute{r}^2\left(\int_0^t C(r',t')\,dt'\right)dr' + \frac{A}{3} + \frac{B}{r^3} \tag{3.27}$$

3.1.3 The generalized expression for radial and hoop stress

Now, after obtaining the generalized expression for radial and hoop strain, we can substitute Eq-(3.26) and Eq-(3.27) in Eq-(3.21) to get the generalized expression for radial stress,

$$\sigma_r(r,t) = -\frac{2E}{3(1-v)}\frac{\Omega}{r^3}\int_{r_0}^{r} r'^2 C(r',t)\,dr' - \frac{2E}{3(1-v)}\frac{\xi\Omega}{r^3}\int_{r_0}^{r} r'^2\left(\int_0^t C(r',t')\,dt'\right)dr' + \frac{AE}{3(1-2v)} - \frac{2BE}{(1+v)r^3} \tag{3.28}$$

$$\sigma_\theta(r,t) = \frac{E\Omega}{3r^3(1-v)}\int_{r_0}^{r} r'^2 C(r',t)\,dr' + \frac{E\xi\Omega}{3r^3(1-v)}\int_{r_0}^{r} r'^2\left(\int_0^t C(r',t')\,dt'\right)dr' + \frac{EA}{3(1-2v)} + \frac{EB}{(1+v)r^3} - \frac{E\Omega C(r,t)}{3(1-v)} - \frac{E\xi\Omega}{3(1-v)}\int_0^t C(r,t')\,dt' \tag{3.29}$$

3.1.4 The Analytical expression of integral constants A and B

Evaluating expressions for A & B using boundary conditions, we get,

$$\sigma_r(r,t) = \left\{\begin{array}{ll} -\frac{2\tau_{resd}}{r_2} - \frac{2K\varepsilon_\theta}{r_2} - \frac{2\gamma}{r_2}, & \text{for } r = r_2 \\ -P, & \text{for } r = r_0 \end{array}\right\} \tag{3.30}$$

Evaluating boundary condition at $r = r_0$, where K is the surface modulus, γ denote the surface energy, τ_{resd} is deformation independent residual stress and -P is the internal pressure at the inner surface of the particle. Due to the nanoscale size of the electrode there exist the Laplace pressure between the pressure of the electrode particle (Hollow silicon particle) and the pressure surrounding the solute atoms (Lithium atoms) during lithiation [38],

$$
\begin{aligned}
-P = -\frac{2E}{3\left(1-v\right)}\frac{\Omega}{{r_0}^3}\int_{r_0}^{r_0} {r'}^2 C\left(r', t\right) dr' - \frac{2E}{3\left(1-v\right)}\frac{\xi\Omega}{{r_0}^3}\int_{r_0}^{r_0} \acute{r}^2 \left(\int_0^t C\left(r', t'\right) dt'\right) r' \\
+ \frac{AE}{3\left(1-2v\right)} - \frac{2BE}{\left(1+v\right){r_0}^3}
\end{aligned}
\tag{3.31}
$$

Rearranging the above expression, we get the relation between A and B

$$
A = \frac{3\left(1-2v\right)}{E}\left(-P + \frac{2BE}{{r_0}^3\left(1+v\right)}\right) \tag{3.32}
$$

Similarly, evaluating boundary condition at $r = r_2$, we get,

$$
\begin{aligned}
B = \frac{2\left(Er_2 - K\left(1+v\right)\right)}{3Z\left(1-v\right)}\frac{\Omega}{{r_2}^4}\int_{r_0}^{r_2} {r'}^2 C\left(r', t\right) dr' + \frac{2\left(Er_2 - K\left(1+v\right)\right)}{3Z\left(1-v\right)}\frac{\xi\Omega}{{r_2}^4}\int_{r_0}^{r_2} \acute{r}^2 \left(\int_0^t C\left(r', t'\right) dt'\right) dr' \\
- \frac{2\gamma}{Zr_2} + \frac{P}{Z}\left(1 + \frac{2K\left(1-2v\right)}{Er_2}\right)
\end{aligned}
\tag{3.33}
$$

Where,

$$
Z = \frac{4K{r_2}^3\left(1-2v\right) + 2K{r_0}^3\left(1+v\right) + 2Er_2\left({r_2}^3 - {r_0}^3\right)}{{r_0}^3{r_2}^4\left(1+v\right)} \tag{3.34}
$$

Similarly, substituting Eq-(3.32) in Eq-(3.33), we get,

$$
\begin{aligned}
A = \frac{4\left(1-2v\right)\left(Er_2 - K\left(1+v\right)\right)}{Z{r_0}^3\left(1+v\right)\left(1-v\right)}\frac{\Omega}{{r_2}^4}\int_{r_0}^{r_2} {r'}^2 C\left(r', t\right) dr' \\
+ \frac{4\left(1-2v\right)\left(Er_2 - K\left(1+v\right)\right)}{Z{r_0}^3\left(1+v\right)\left(1-v\right)}\frac{\xi\Omega}{{r_2}^4}\int_{r_0}^{r_2} \acute{r}^2 \left(\int_0^t C\left(r', t'\right) dt'\right) dr' - \frac{12\gamma\left(1-2v\right)}{Zr_2{r_0}^3\left(1+v\right)} \\
+ \frac{6P\left(1-2v\right)}{Z{r_0}^3\left(1+v\right)}\left(1 + \frac{2K\left(1-2v\right)}{Er_2}\right) - \frac{3P\left(1-2v\right)}{E}
\end{aligned}
\tag{3.35}
$$

3.1.5 Analytical expression for radial and hoop stress

After obtaining the expression for A and B from Eq-(3.35) and Eq-(3.33) respectively, we can now substitute it to Eq-(3.28) to get the final analytical expression of radial stress for the hollow spherical particle.

$$\begin{aligned}
\sigma_r(r,t) &= -\frac{2E}{3(1-v)}\frac{\Omega}{r^3}\int_{r_0}^{r} r'^2 C(r',t)\,dr' - \frac{2E}{3(1-v)}\frac{\xi\Omega}{r^3}\int_{r_0}^{r} r'^2\left(\int_0^t C(r',t')\,dt'\right)dr' \\
&+ \frac{2E\Omega\left(Er_2 - K(1+v)\right)\left(r^3 - {r_0}^3\right)}{3r^3\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)(1-v)}\int_{r_0}^{r_2} r'^2 C(r',t)\,dr' \\
&+ \frac{2E\xi\Omega\left(Er_2 - K(1+v)\right)\left(r^3 - {r_0}^3\right)}{3r^3\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)(1-v)}\int_{r_0}^{r_2} r'^2\left(\int_0^t C(r',t')\,dt'\right)dr' \\
&- \frac{2E\gamma\left(r^3 - {r_0}^3\right){r_2}^3}{r^3\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)} \\
&+ P\left\{\frac{\left(Er_2 + 2K(1-2v)\right)\left(r^3 - {r_0}^3\right){r_2}^3}{r^3\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)} - 1\right\}
\end{aligned} \tag{3.36}$$

Similarly, substituting Eq-(3.35) and Eq-(3.33) in Eq-(3.29) to get the analytical expression for hoop stress

$$\begin{aligned}
\sigma_\theta(r,t) &= \frac{E\Omega}{3r^3(1-v)}\int_{r_0}^{r} r'^2 C(r',t)\,dr' + \frac{E\xi\Omega}{3r^3(1-v)}\int_{r_0}^{r} r'^2\left(\int_0^t C(r',t')\,dt'\right)dr' \\
&+ \frac{E\Omega\left(Er_2 - K(1+v)\right)\left(2r^3 + {r_0}^3\right)}{3r^3\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)(1-v)}\int_{r_0}^{r_2} r'^2 C(r',t)\,dr' \\
&+ \frac{E\xi\Omega\left(Er_2 - K(1+v)\right)\left(2r^3 + {r_0}^3\right)}{3r^3\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)(1-v)}\int_{r_0}^{r_2} r'^2\left(\int_0^t C(r',t')\,dt'\right)dr' \\
&- \frac{E\gamma\left(2r^3 + {r_0}^3\right){r_2}^3}{r^3\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)} \\
&+ P\left\{\frac{\left(Er_2 + 2K(1-2v)\right)\left(2r^3 + {r_0}^3\right){r_2}^3}{r^3\left(4K{r_2}^3(1-2v) + 2K{r_0}^3(1+v) + 2Er_2\left({r_2}^3 - {r_0}^3\right)\right)} - 1\right\} \\
&- \frac{E\Omega C(r,t)}{3(1-v)} - \frac{E\xi\Omega}{3(1-v)}\int_0^t C(r,t')\,dt'
\end{aligned} \tag{3.37}$$

3.1.6 Analytical expression for hydrostatic stress

Hydrostatic stress (mean stress) is defined as given by Eq-(3.38), where $\sigma_\theta(r,t) = \sigma_\phi(r,t)$ due to spherical symmetry [43]

$$\sigma_h(r,t) = \frac{(\sigma_r(r,t) + 2\sigma_\theta(r,t))}{3} \tag{3.38}$$

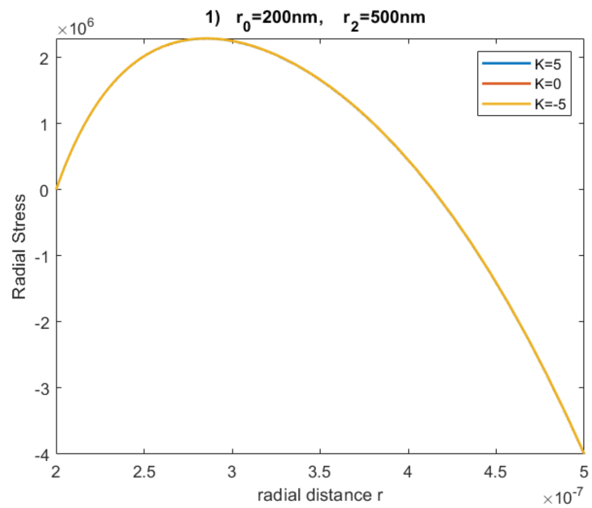
Substituting the obtained analytical expressions for radial and hoop stress in Eq-(3.38), we get,

$$\begin{aligned}
\sigma_h(r,t) = &\frac{2E\Omega\left(Er_2 - K(1+v)\right)}{3\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)(1-v)} \int_{r_0}^{r_2} r'^2 C(r',t)\,dr' \\
&+ \frac{2E\xi\Omega\left(Er_2 - K(1+v)\right)}{3\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)(1-v)} \int_{r_0}^{r_2} r'^2 \left(\int_0^t C(r',t')\,dt'\right) dr' \\
&- \frac{2E\gamma {r_2}^3}{\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)} \\
&+ P\left\{\frac{\left(Er_2 + 2K(1-2v)\right){r_2}^3}{\left(2K{r_2}^3(1-2v) + K{r_0}^3(1+v) + Er_2\left({r_2}^3 - {r_0}^3\right)\right)} - 1\right\} \\
&- \frac{2E\Omega C(r,t)}{9(1-v)} - \frac{2E\xi\Omega}{9(1-v)} \int_0^t C(r,t')\,dt'
\end{aligned} \tag{3.39}$$

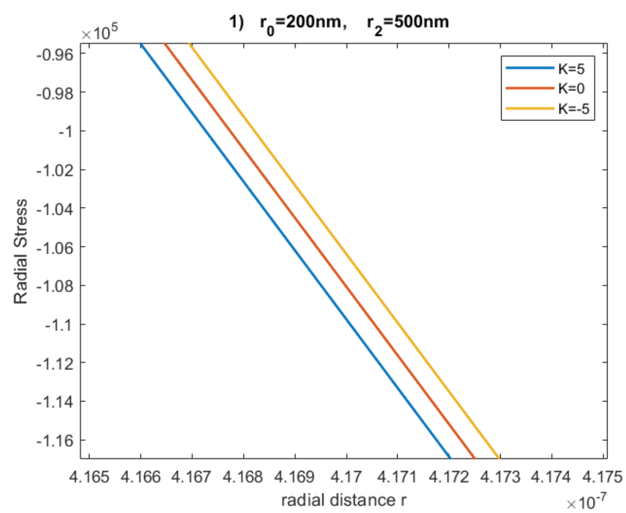
In summary, for the above derivations. Analytical expressions for all the stresses have been computed, Eq-(3.36), Eq-(3.37) and Eq-(3.39) are radial, hoop (tangential), and hyrdostatic (mean) stress respectively acting on the hollow silicon particle due to the intercalation of the lithium atoms. As far as the material properties of the particle are considered, Poisson's ratio is independent of the concentration whereas, Young's modulus mainly depend upon the stoichiometric (concentration) ratio of lithium bonded with silicon due the formation of Li_xSi_y alloy ($X = \frac{x}{y}$), thus Young's modulus E of the pure silicon may change during lithiation process as $\acute{E} = E(1 + \eta_E X_{max} c)$, where E is the Young's modulus of pure silicon, η_E is the Rate of change of elastic modulus respect to concentration c, and X_{max} represents the maximum saturation of lithium in alloy [37]. The alloying of lithium with host atoms (Silicon) is typically an amorphous in nature. Experimental and theoretical analysis [44] [45] [46] shows that there must be minimum value of X must be reached which is approximately X= 0.2 in order to form an amorphous alloy [37]. Once the above threshold value reach more lithium atoms will diffuse into the particle to form $\mathrm{Li}_x\mathrm{Si}_y$ alloy. The dependence of Young's modulus on the concentration c (Non-dimensional quantity) is the ratio of X to the maximum saturation of lithium in Li_xSi_y alloy ($c = X/X_{max}$) [47], substituting the ratio into the above expression of Young's modulus (Concentration dependency) lead to $\acute{E} = E\,(1 + \eta_E X)$, therefore as the reaction progresses the elastic modulus of the lithiated silicon will change. Surface effects or surface constitutive relationship has been used to study the size dependent mechanical behaviors of nano-materials and nano-structures [48] [49], in this work we employ Gurtin-Murdoch theory [50] to study the interface effects of lithium intercalating with silicon in case of hollow spherical particle. In order to evaluate the expression for A and B surface effects has been considered at the outer radius of the hollow particle keeping τ_{rs} deformation independent residual stress equals to zero.

3.2 Graphical analysis of radial, hoop, hydrostatic stress

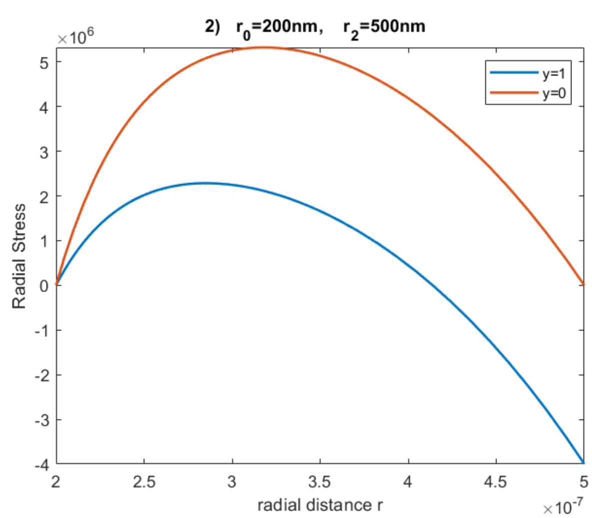
The parameters given in the Table-(3.1) were used to compute radial, hoop and hydrostatic stresses for hollow spherical particle (r_0 is the inner radius and r_2 is the outer radius) through MATLAB, whereas the equations have been verified with MATHEMATICA. Fig-(3.6) shows the variation in radial stress acting on the particle by varying different parameters like K, γ, ξ and time over the wide range of inner and outer radius of the silicon hollow sphere. Fig- (3.11) shows the variation in hoop stress similarly, Fig-(3.16) shows the variation in hydrostatic stress and Fig- (3.21) shows the variation in the difference of radial and hoop stress $(\sigma_r\,(r,t) - \sigma_\theta\,(r,t))$ under the elastic region. While performing the simulations internal compressive pressure -P acting on the inner surface of the hollow spherical particle is considered to be zero. For the simplicity of the model Young's modulus of the particle is considered to be constant throughout the computation.


1) r0=200nm, r2=500nm
×10^6
Radial Stress
radial distance r
×10^-7
K=5
K=0
K=-5

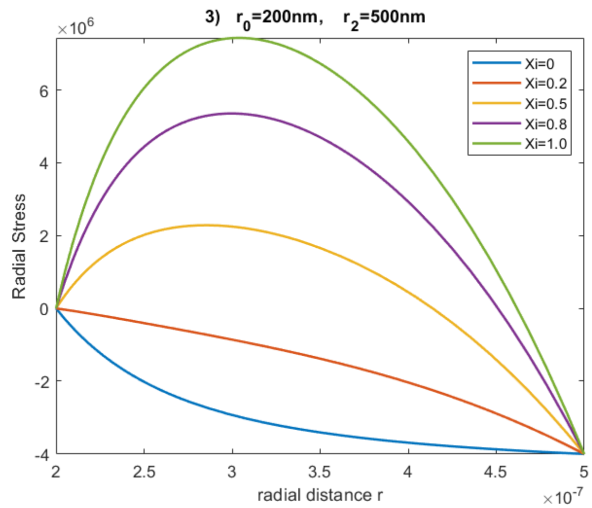
(a)


1) r0=200nm, r2=500nm
×10^5
Radial Stress
radial distance r
×10^-7
K=5
K=0
K=-5

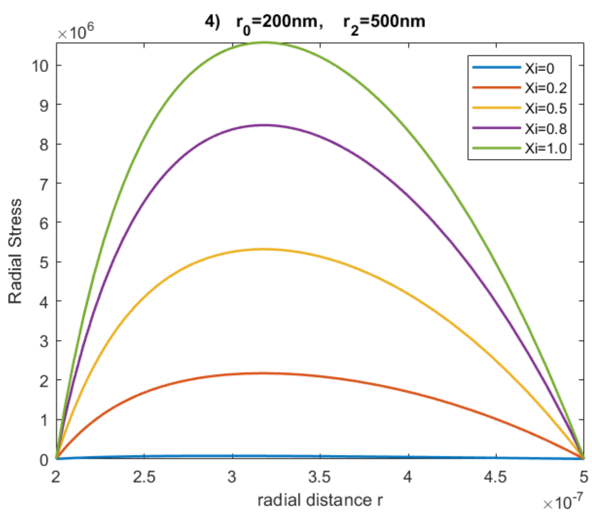
(b)


2) r0=200nm, r2=500nm
×10^6
Radial Stress
radial distance r
×10^-7
y=1
y=0

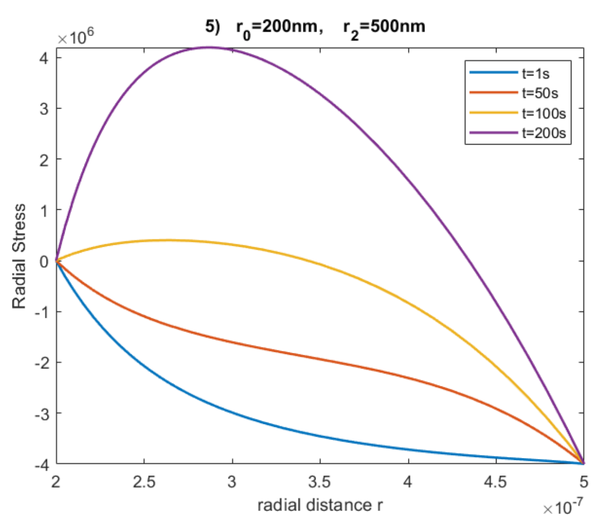
(c)



(d)

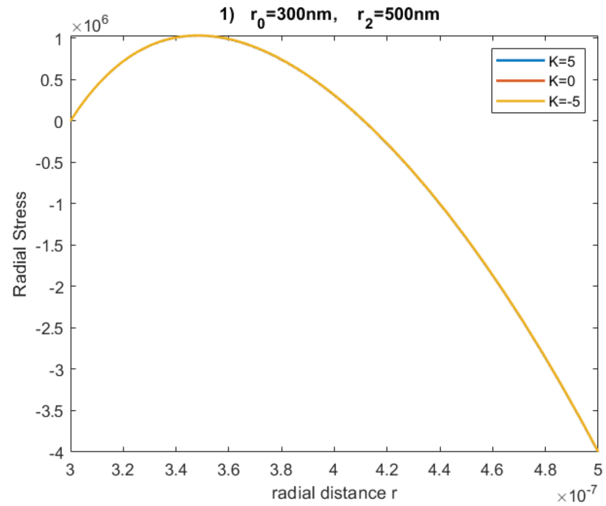


(e)

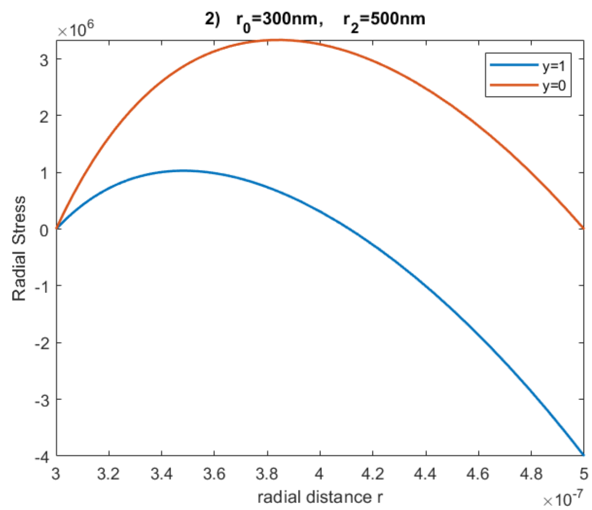


(f)

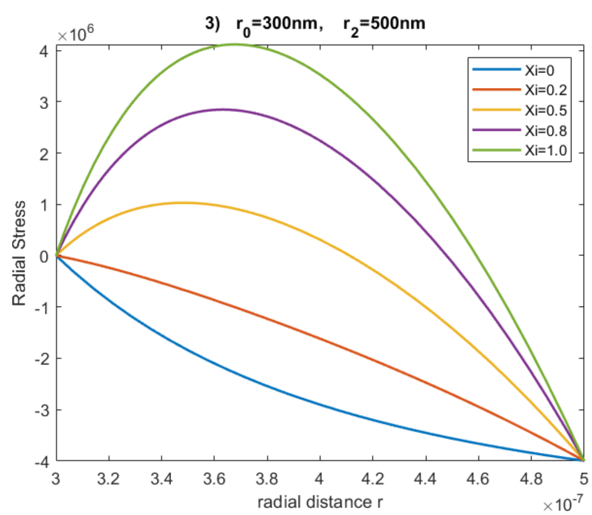
Figure 3.2: (a) Radial stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying surface modulus K, (b) Distinguishing Radial stress with different values of surface modulus K, (c) Radial stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying surface energy γ, (d) Radial stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying ξ keeping γ equal to 1, (e) Radial stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying ξ keeping γ equal to 0 , (f) Radial Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying time


1) r_0=300nm, r_2=500nm
×10^6
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
Radial Stress
3
3.2
3.4
3.6
3.8
4
4.2
4.4
4.6
4.8
5
radial distance r
×10^-7
K=5
K=0
K=-5

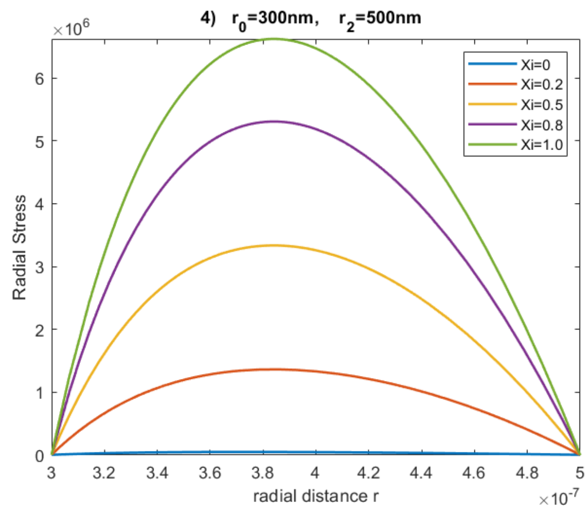
(a)


2) r_0=300nm, r_2=500nm
×10^6
3
2
1
0
-1
-2
-3
-4
Radial Stress
3
3.2
3.4
3.6
3.8
4
4.2
4.4
4.6
4.8
5
radial distance r
×10^-7
y=1
y=0

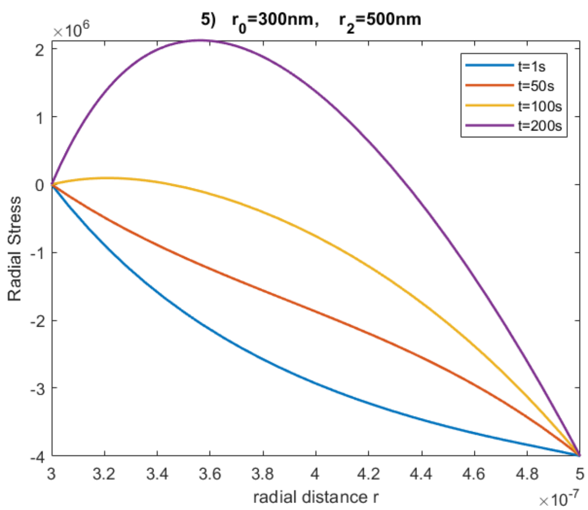
(b)


3) r_0=300nm, r_2=500nm
×10^6
4
3
2
1
0
-1
-2
-3
-4
Radial Stress
3
3.2
3.4
3.6
3.8
4
4.2
4.4
4.6
4.8
5
radial distance r
×10^-7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0

(c)

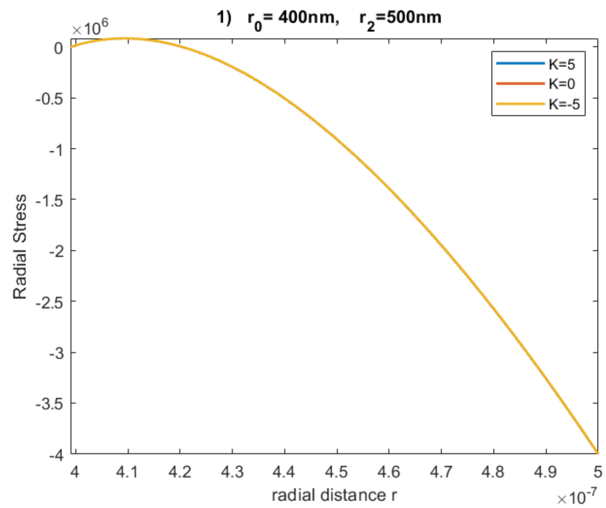


(d)

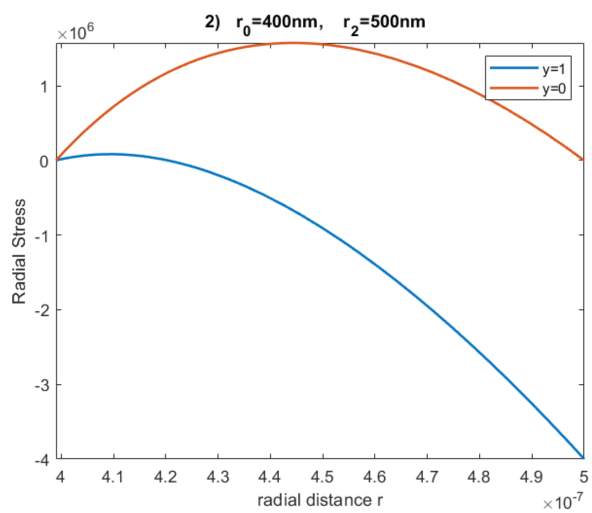


(e)

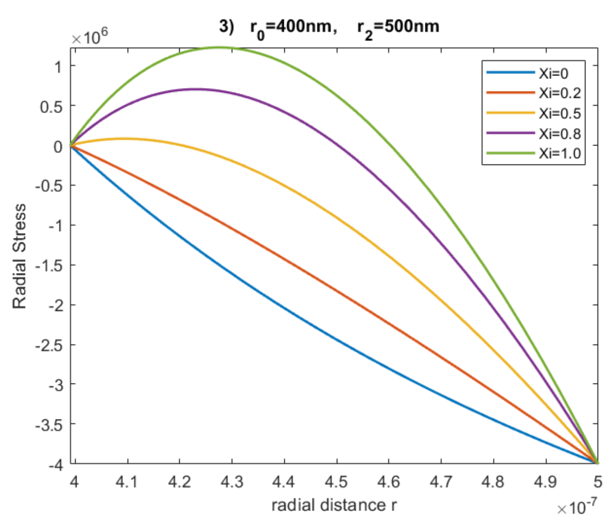
Figure 3.3: (a) Radial stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface modulus K Radial stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface energy γ, (c) Radial stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 1, (d) Radial stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 0, (e) Radial stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying time


1) r_0= 400nm, r_2=500nm
×10^6
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
Radial Stress
K=5
K=0
K=-5
4 4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8 4.9 5
radial distance r
×10^-7

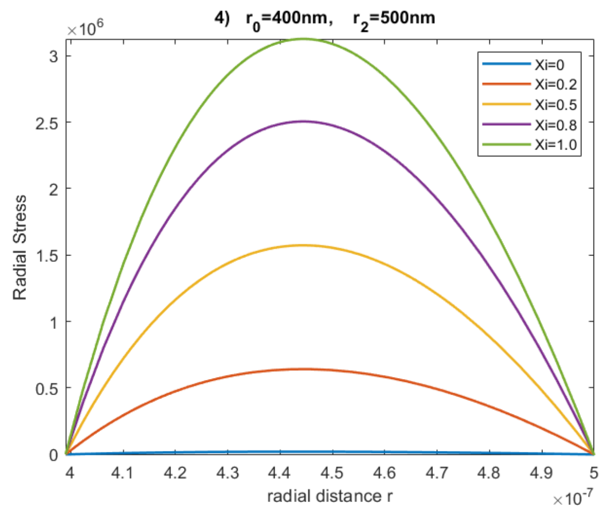
(a)


2) r_0=400nm, r_2=500nm
×10^6
1
0
-1
-2
-3
-4
Radial Stress
y=1
y=0
4 4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8 4.9 5
radial distance r
×10^-7

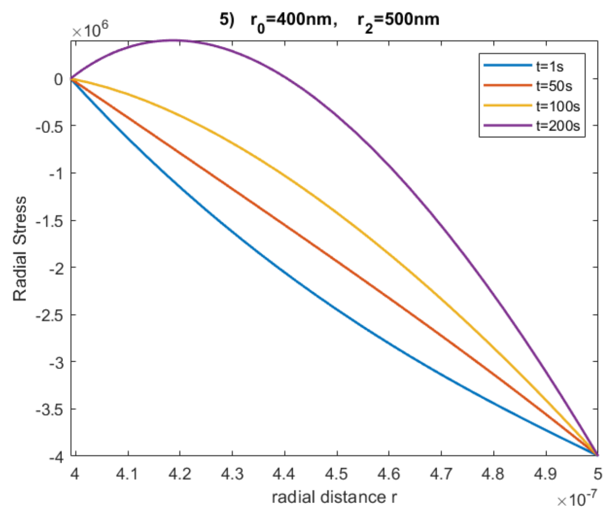
(b)


3) r_0=400nm, r_2=500nm
×10^6
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
Radial Stress
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
4 4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8 4.9 5
radial distance r
×10^-7

(c)

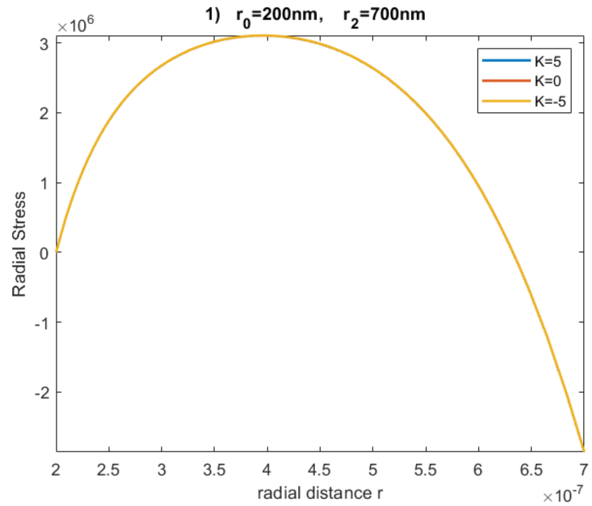


(d)

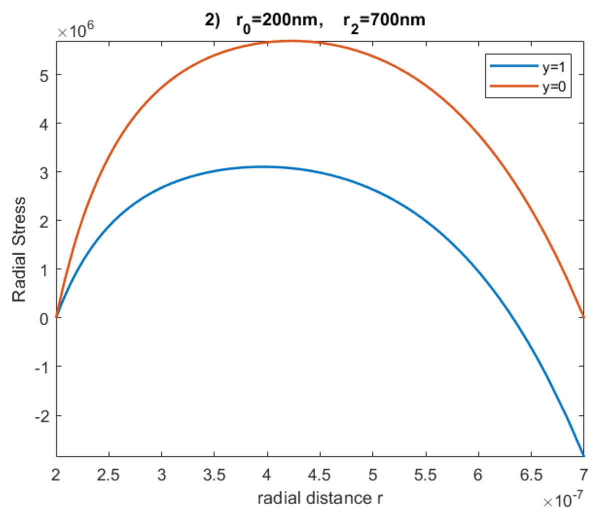


(e)

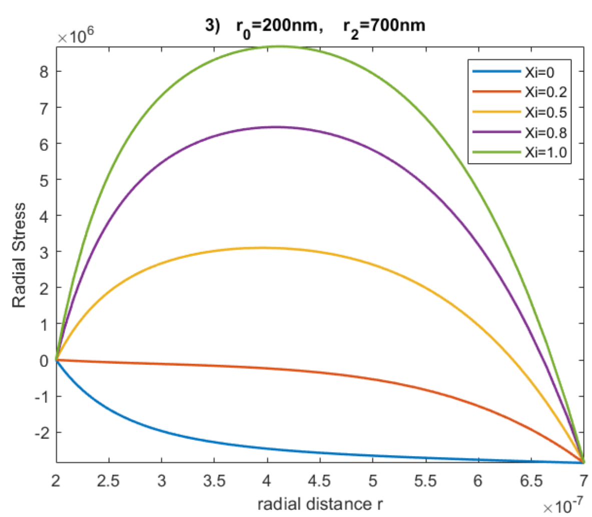
Figure 3.4: (a) Radial stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying surface modulus K, (b) Radial stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying surface energy γ, (c) Radial stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying ξ keeping γ equal to 1, (d) Radial stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying ξ keeping γ equal to 0, (e) Radial stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying time


1) r_0=200nm, r_2=700nm
×10^6
3
2
1
0
-1
-2
Radial Stress
K=5
K=0
K=-5
2 2.5 3 3.5 4 4.5 5 5.5 6 6.5 7
radial distance r
×10^-7

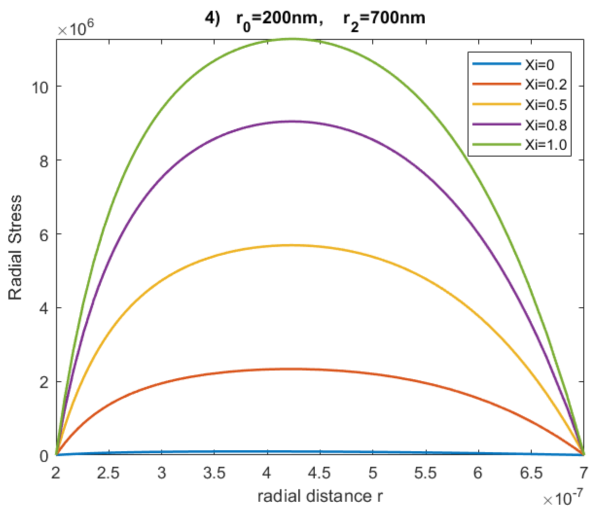
(a)


2) r_0=200nm, r_2=700nm
×10^6
5
4
3
2
1
0
-1
-2
Radial Stress
y=1
y=0
2 2.5 3 3.5 4 4.5 5 5.5 6 6.5 7
radial distance r
×10^-7

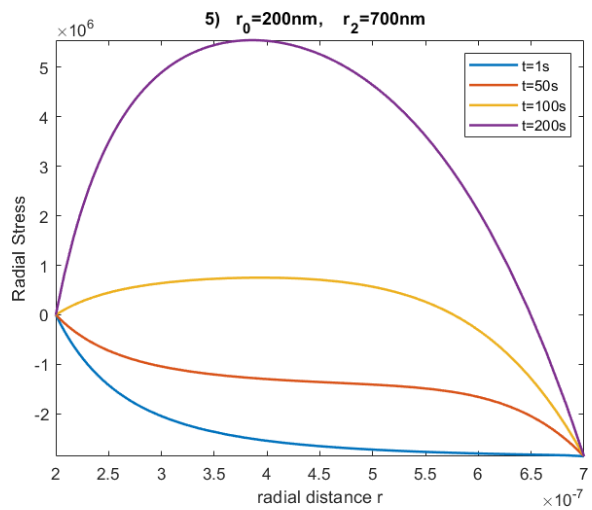
(b)


3) r_0=200nm, r_2=700nm
×10^6
8
7
6
5
4
3
2
1
0
-1
-2
Radial Stress
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
2 2.5 3 3.5 4 4.5 5 5.5 6 6.5 7
radial distance r
×10^-7

(c)

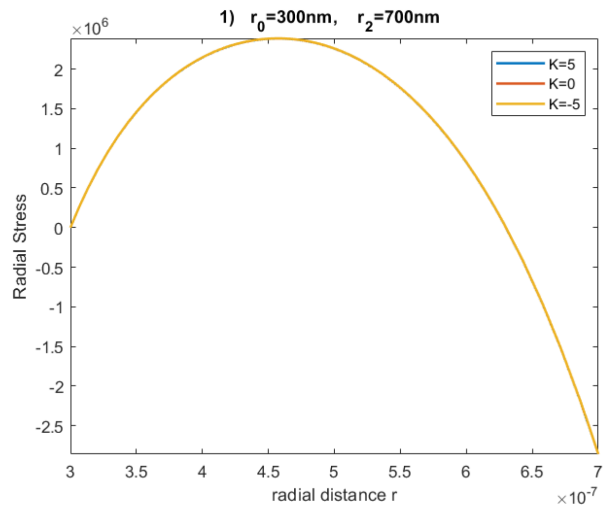


(d)

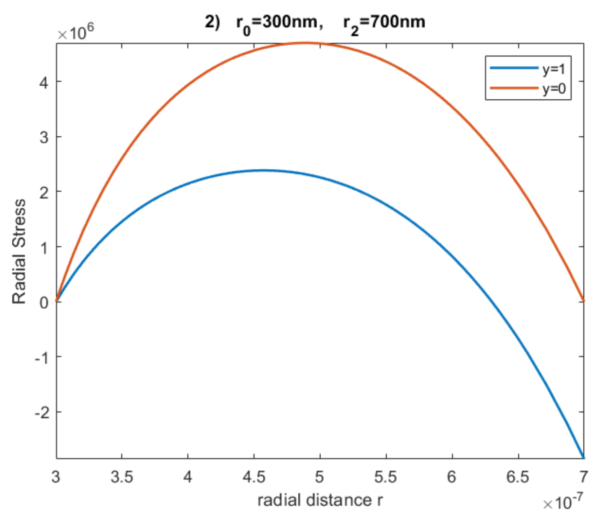


(e)

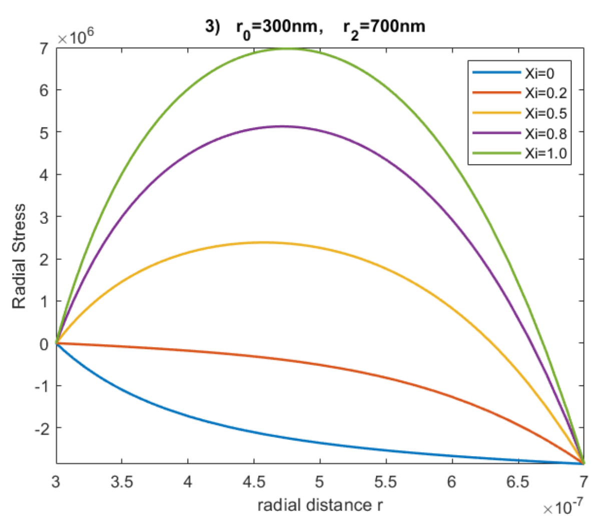
Figure 3.5: (a) Radial stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying surface modulus K, (b) Radial stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying surface energy γ, (c) Radial stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying ξ keeping γ equal to 1, (d) Radial stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying ξ keeping γ equal to 0, (e) Radial stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying time


1) r0=300nm, r2=700nm
×10^6
K=5
K=0
K=-5
Radial Stress
radial distance r
×10^-7

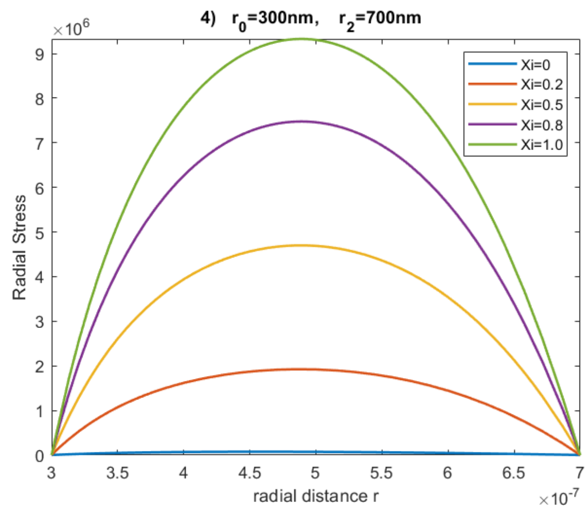
(a)


2) r0=300nm, r2=700nm
×10^6
y=1
y=0
Radial Stress
radial distance r
×10^-7

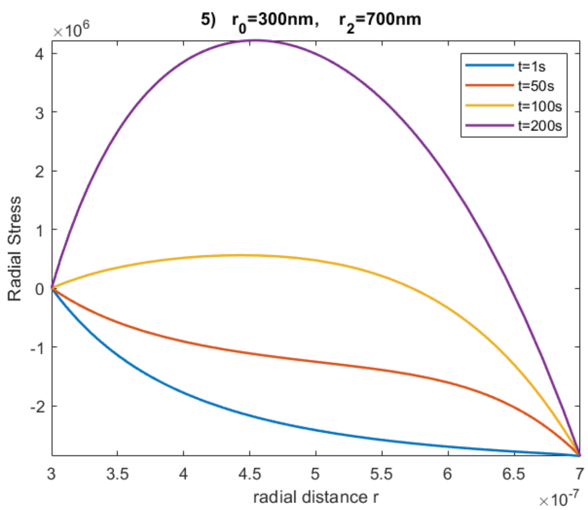
(b)


3) r0=300nm, r2=700nm
×10^6
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
Radial Stress
radial distance r
×10^-7

(c)

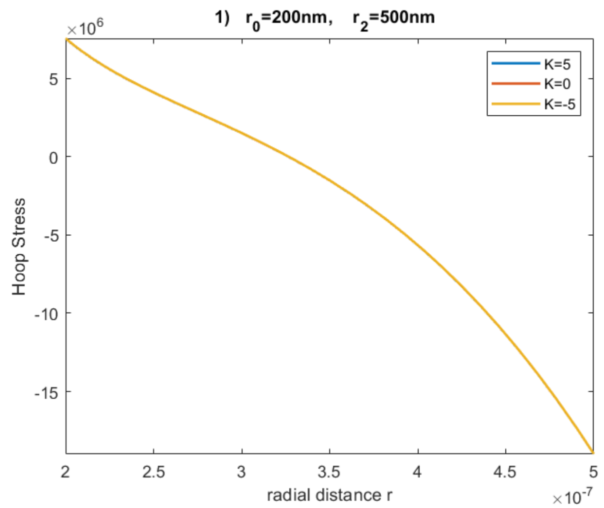


(d)

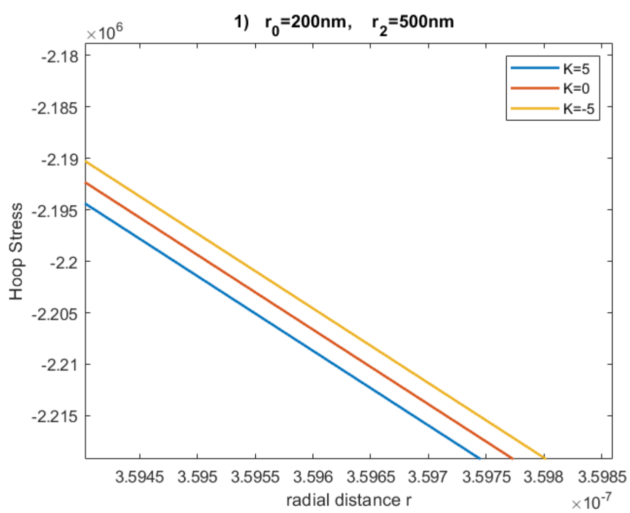


(e)

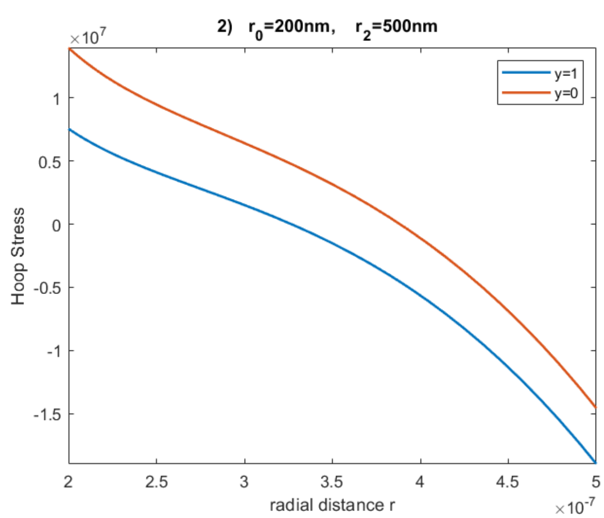
Figure 3.6: (a) Radial stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying surface modulus K, (b) Radial stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying surface energy γ, (c) Radial stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying ξ keeping γ equal to 1, (d) Radial stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying ξ keeping γ equal to 0, (e) Radial stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying time


1) r_0=200nm, r_2=500nm
Hoop Stress
radial distance r
K=5
K=0
K=-5

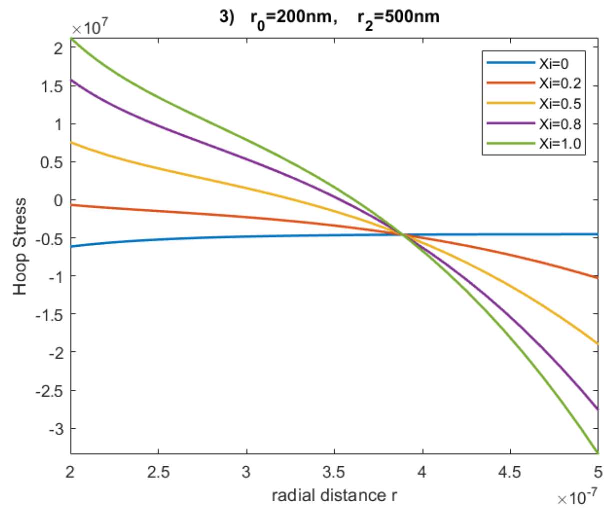
(a)


1) r_0=200nm, r_2=500nm
Hoop Stress
radial distance r
K=5
K=0
K=-5

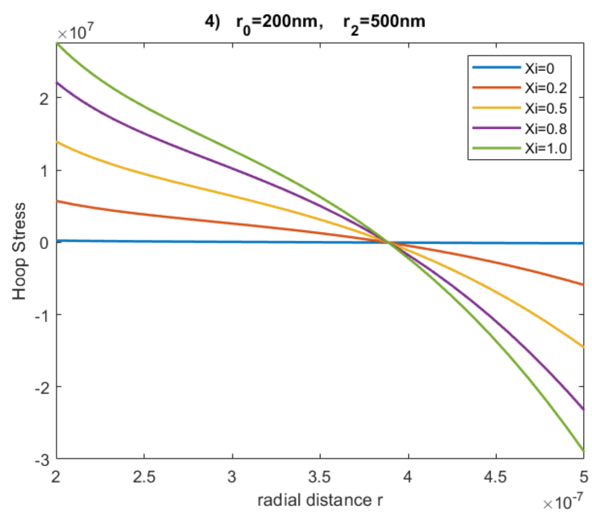
(b)


2) r_0=200nm, r_2=500nm
Hoop Stress
radial distance r
y=1
y=0

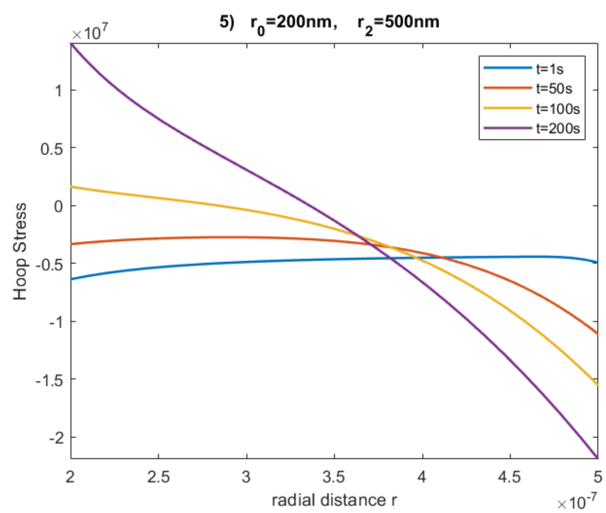
(c)



(d)

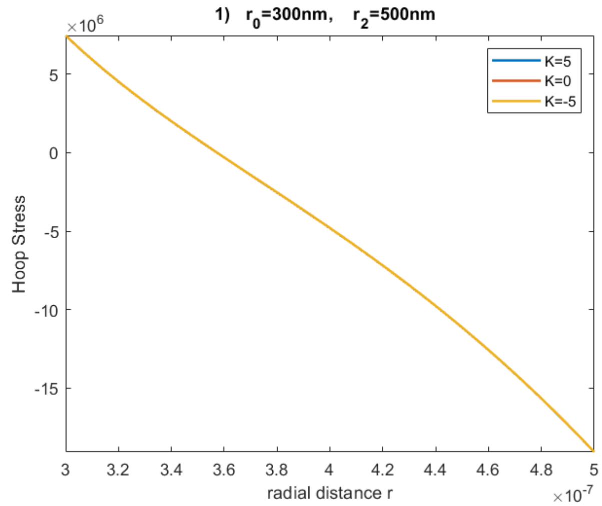


(e)

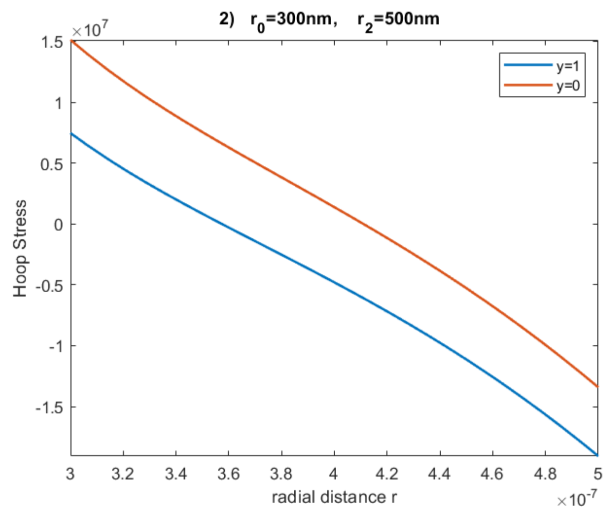


(f)

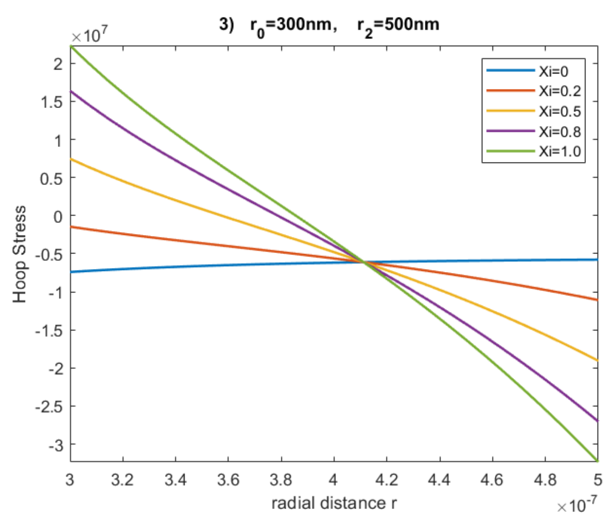
Figure 3.7: (a) Hoop stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying surface modulus K, (b) Distinguishing Hoop stress with different values of surface modulus K, (c) Hoop stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying surface energy γ, (d) Hoop stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying ξ keeping γ equal to 1, (e) Hoop stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying ξ keeping γ equal to 0, (f) Hoop Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying time


1) r0=300nm, r2=500nm
×10^6
K=5
K=0
K=-5
Hoop Stress
radial distance r
×10^-7

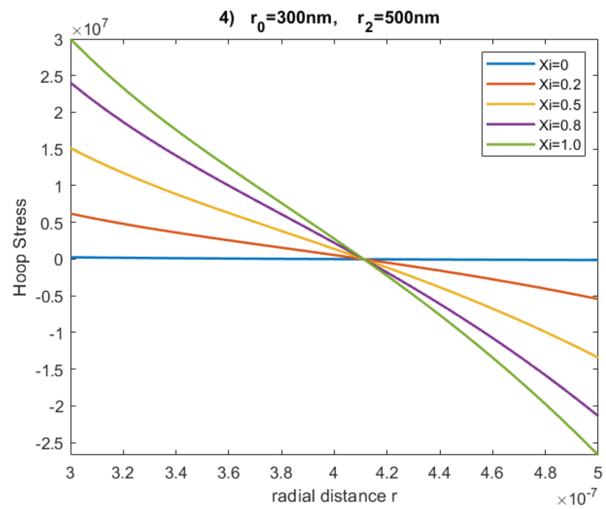
(a)


2) r0=300nm, r2=500nm
×10^7
y=1
y=0
Hoop Stress
radial distance r
×10^-7

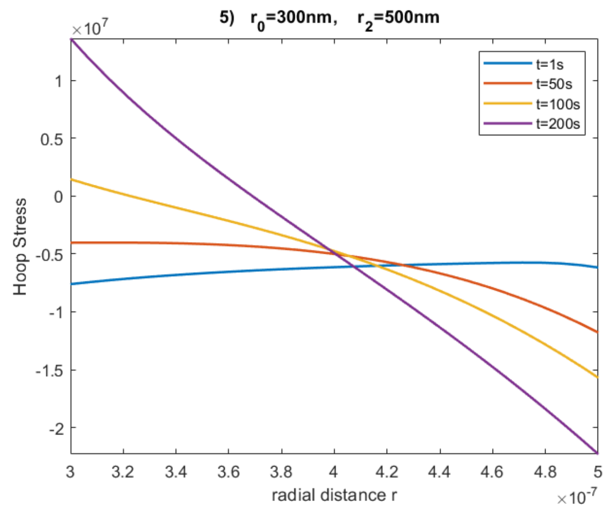
(b)


3) r0=300nm, r2=500nm
×10^7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
Hoop Stress
radial distance r
×10^-7

(c)

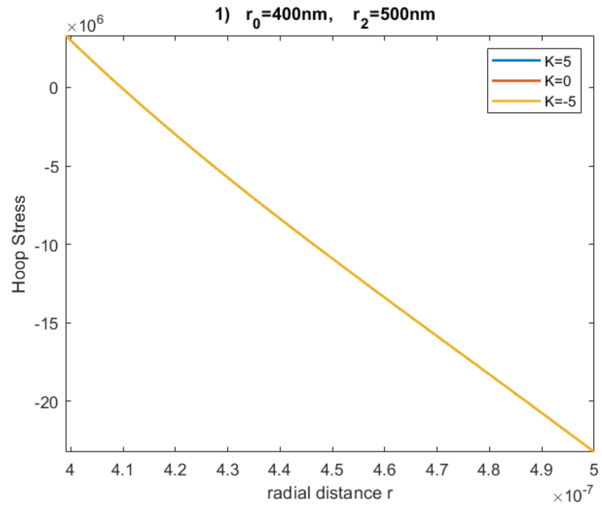


(d)

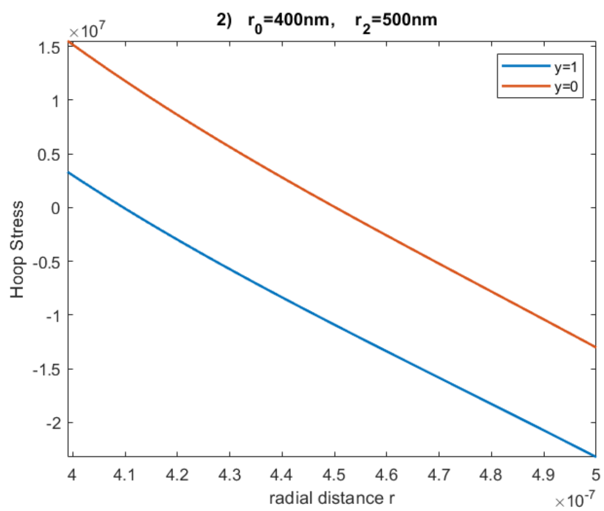


(e)

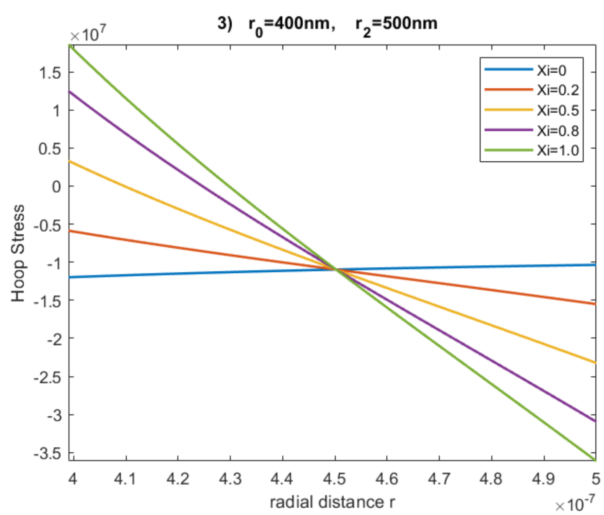
Figure 3.8: (a) Hoop stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface modulus K, (b) Hoop stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface energy γ, (c) Hoop stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 1, (d) Hoop stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 0, (e) Hoop stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying time


1) r0=400nm, r2=500nm
×10^6
K=5
K=0
K=-5
Hoop Stress
radial distance r
×10^-7

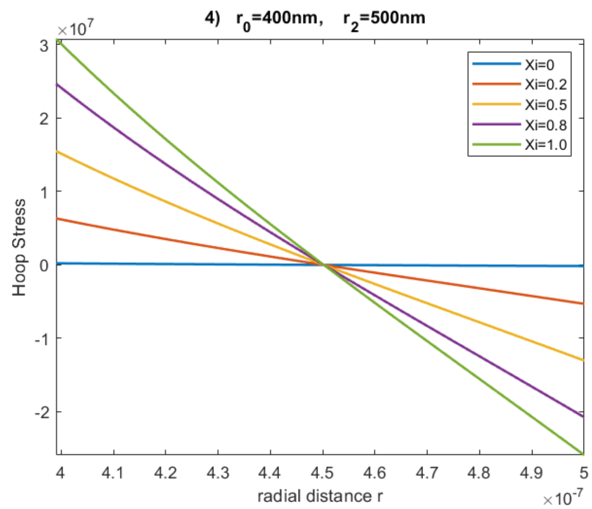
(a)


2) r0=400nm, r2=500nm
×10^7
y=1
y=0
Hoop Stress
radial distance r
×10^-7

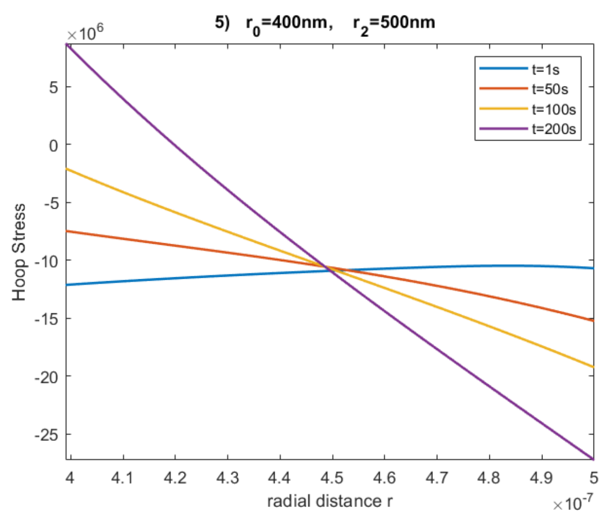
(b)


3) r0=400nm, r2=500nm
×10^7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
Hoop Stress
radial distance r
×10^-7

(c)

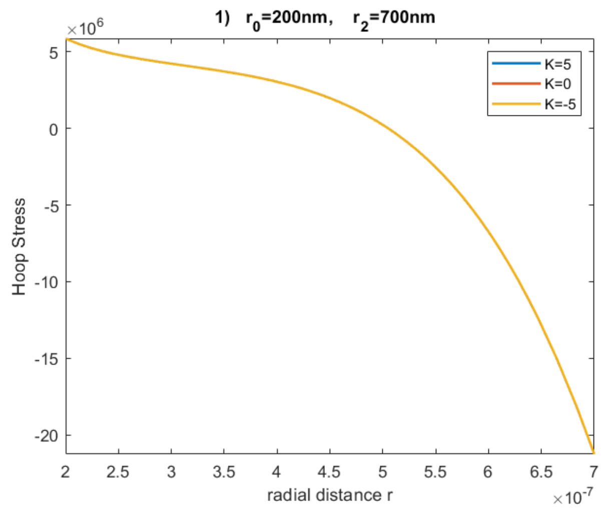


(d)

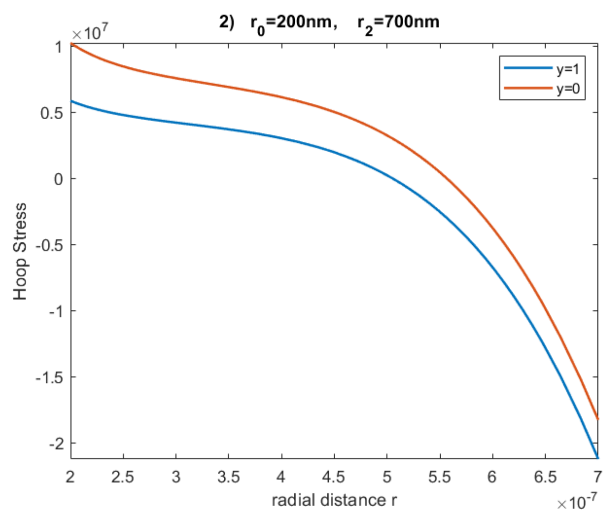


(e)

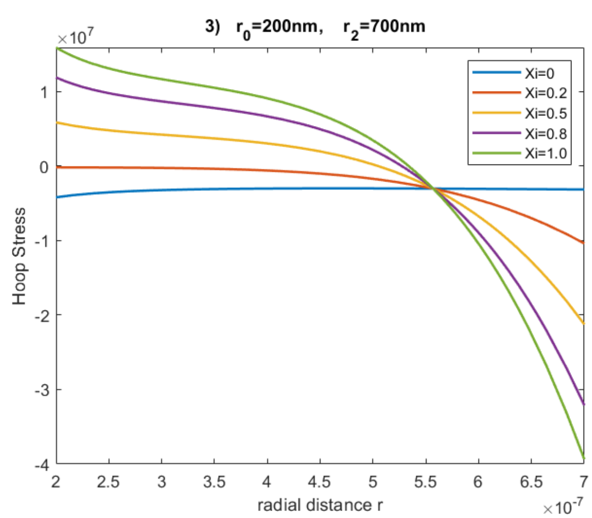
Figure 3.9: (a) Hoop stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying surface modulus K, (b) Hoop stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying surface energy γ, (c) Hoop stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying ξ keeping γ equal to 1, (d) Hoop stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying ξ keeping γ equal to 0, (e) Hoop stress Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying time


1) r0=200nm, r2=700nm
×10^6
Hoop Stress
radial distance r
×10^-7
K=5
K=0
K=-5

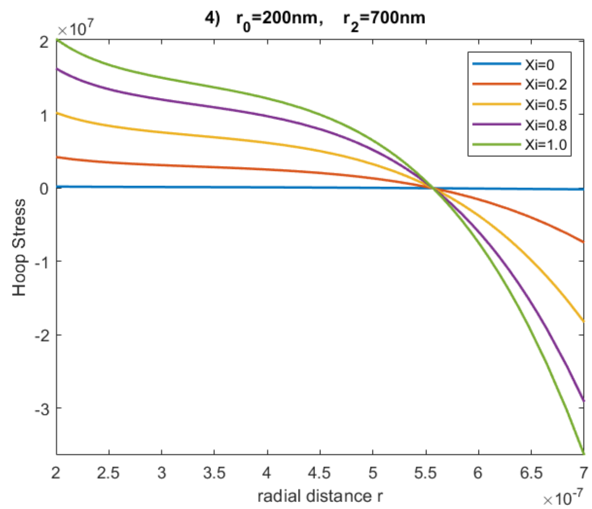
(a)


2) r0=200nm, r2=700nm
×10^7
Hoop Stress
radial distance r
×10^-7
y=1
y=0

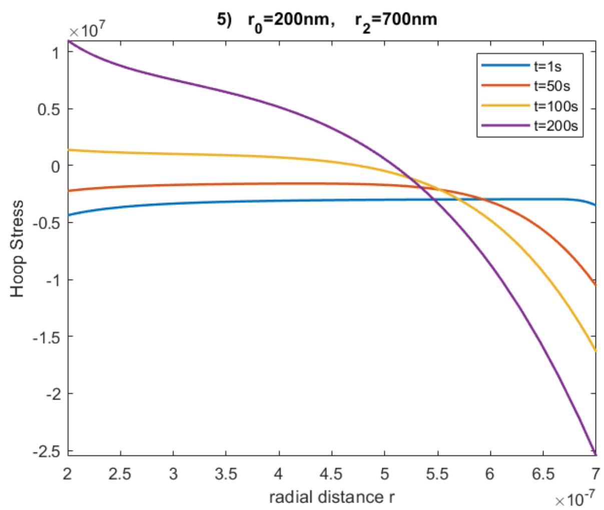
(b)


3) r0=200nm, r2=700nm
×10^7
Hoop Stress
radial distance r
×10^-7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0

(c)

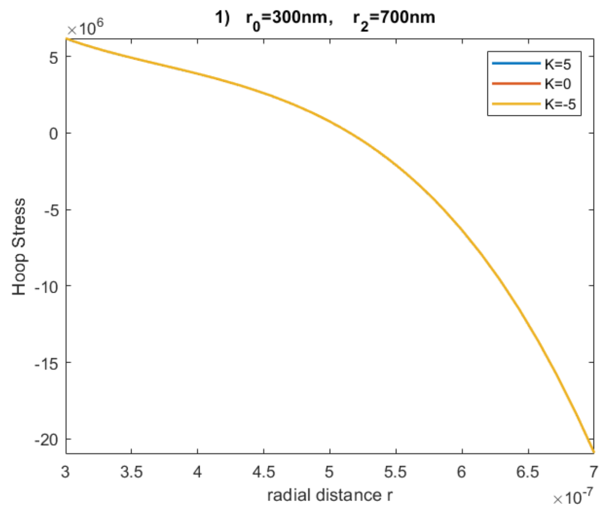


(d)



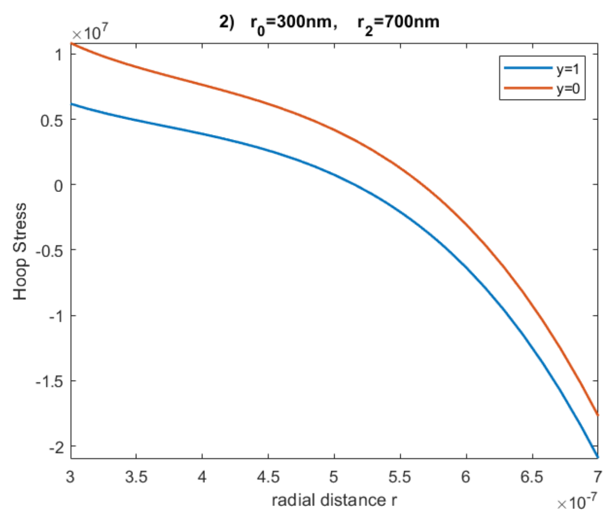
(e)

Figure 3.10: (a) Hoop stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying surface modulus K, (b) Hoop stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying surface energy γ, (c) Hoop stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying ξ keeping γ equal to 1, (d) Hoop stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying ξ keeping γ equal to 0, (e) Hoop stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying time



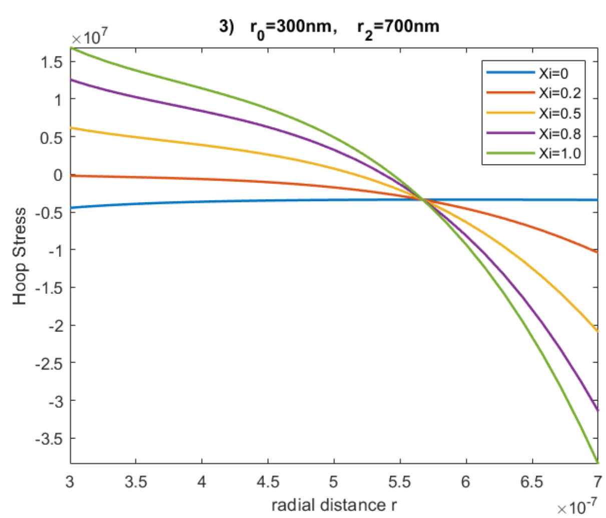
1) r_0=300nm, r_2=700nm
×10^6
Hoop Stress
radial distance r
×10^-7
K=5
K=0
K=-5

(a)



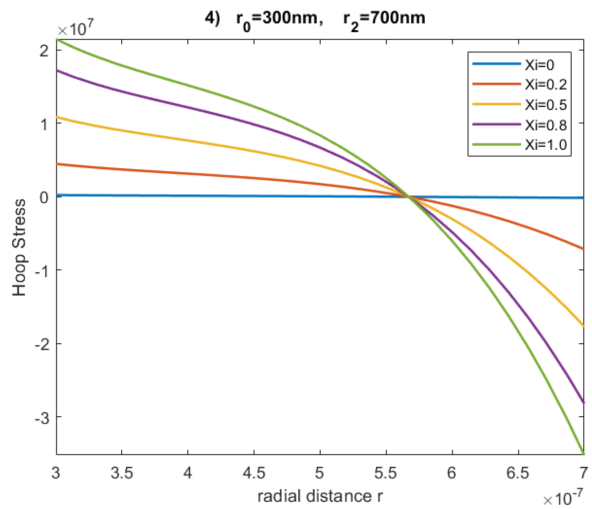
2) r_0=300nm, r_2=700nm
×10^7
Hoop Stress
radial distance r
×10^-7
y=1
y=0

(b)

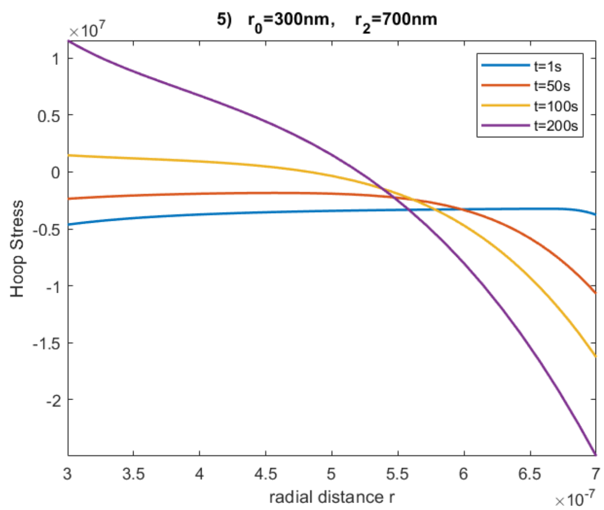


3) r_0=300nm, r_2=700nm
×10^7
Hoop Stress
radial distance r
×10^-7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0

(c)

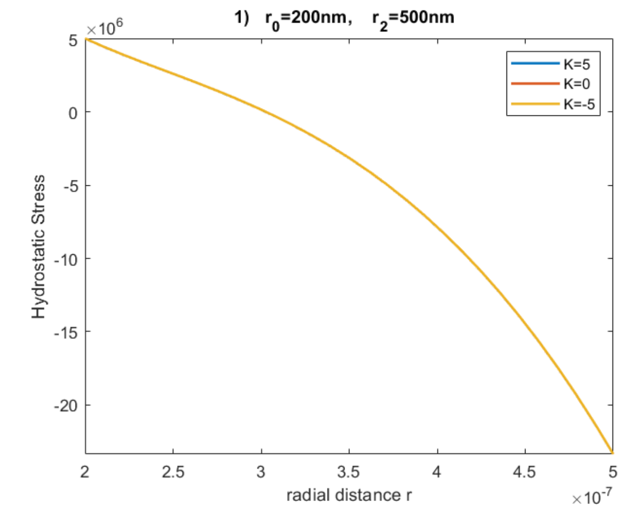


(d)

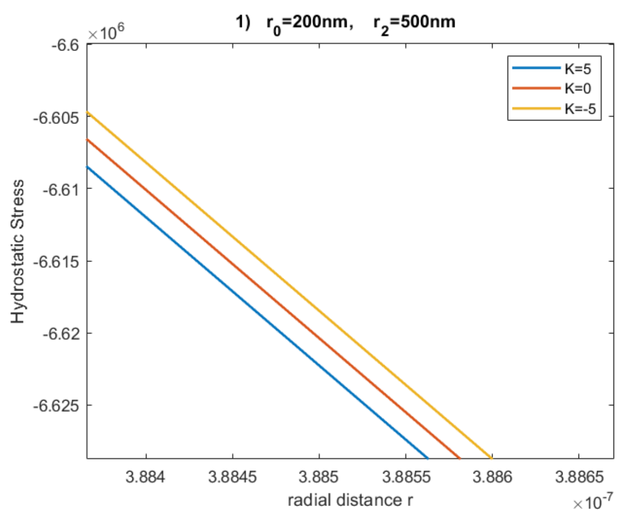


(e)

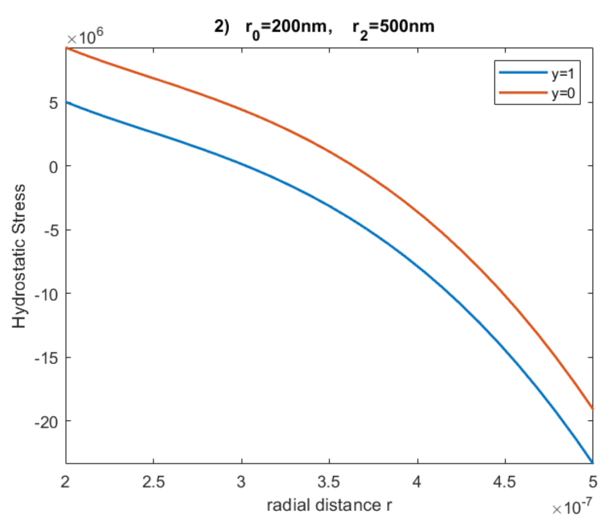
Figure 3.11: (a) Hoop stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying surface modulus K, (b) Hoop stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying surface energy γ, (c) Hoop stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying ξ keeping γ equal to 1, (d) Hoop stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying ξ keeping γ equal to 0, (e) Hoop stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying time


1) r0=200nm, r2=500nm
×10^6
5
0
-5
-10
-15
-20
Hydrostatic Stress
K=5
K=0
K=-5
2
2.5
3
3.5
4
4.5
5
radial distance r
×10^-7

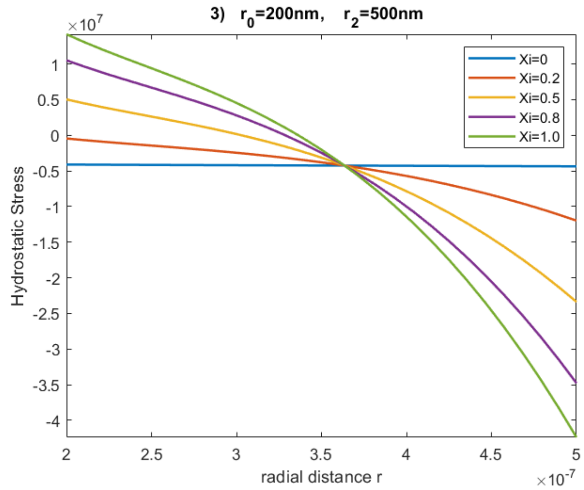
(a)


1) r0=200nm, r2=500nm
×10^6
-6.6
-6.605
-6.61
-6.615
-6.62
-6.625
Hydrostatic Stress
K=5
K=0
K=-5
3.884
3.8845
3.885
3.8855
3.886
3.8865
radial distance r
×10^-7

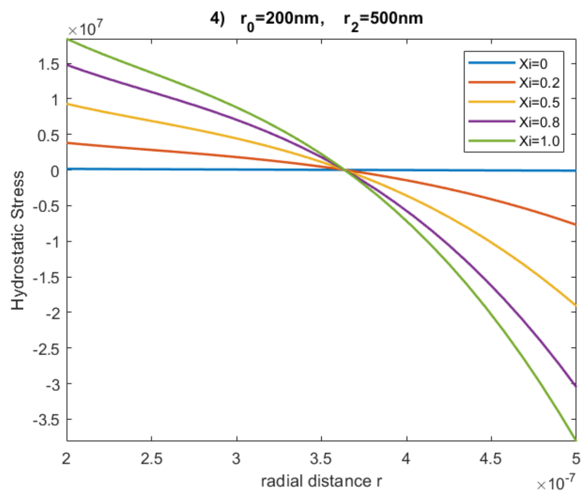
(b)


2) r0=200nm, r2=500nm
×10^6
5
0
-5
-10
-15
-20
Hydrostatic Stress
y=1
y=0
2
2.5
3
3.5
4
4.5
5
radial distance r
×10^-7

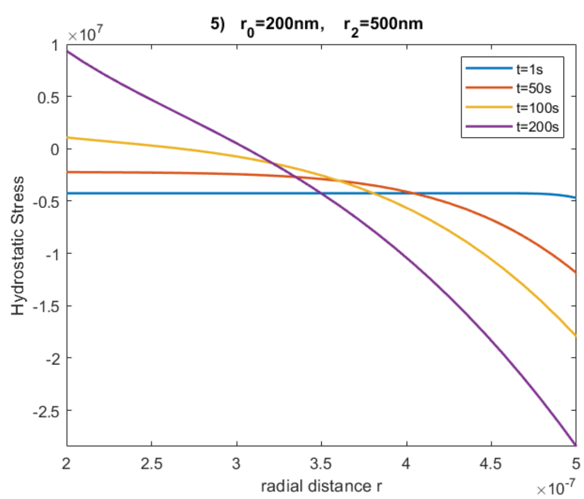
(c)



(d)

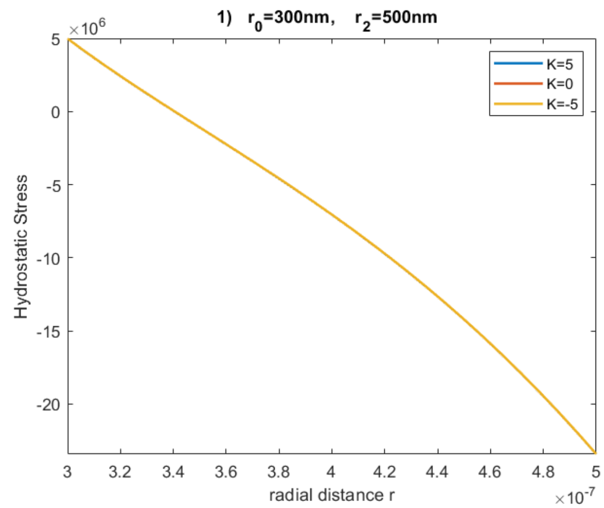


(e)

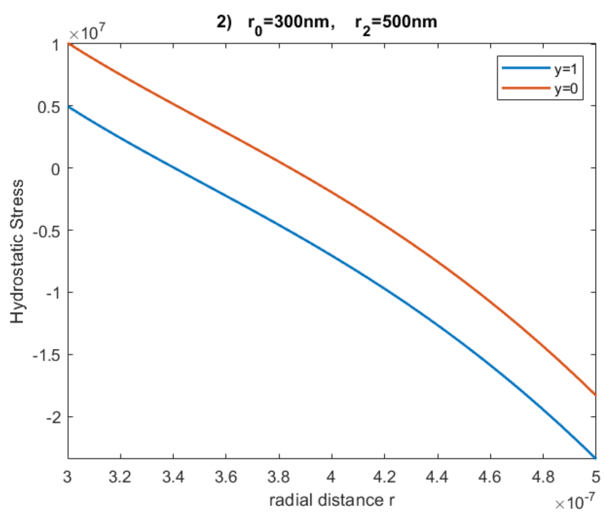


(f)

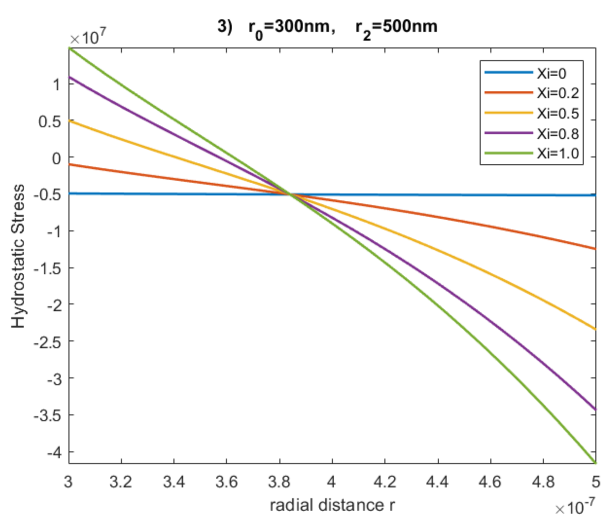
Figure 3.12: (a) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying surface modulus K, (b) Distinguishing Hydrostatic stress with different values of surface modulus K, (c) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying surface energy γ, (d) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying ξ keeping γ equal to 1, (e) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying ξ keeping γ equal to 0 , (f) Hydrostatic Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying time


1) r0=300nm, r2=500nm
×10^6
5
0
-5
-10
-15
-20
Hydrostatic Stress
K=5
K=0
K=-5
3
3.2
3.4
3.6
3.8
4
4.2
4.4
4.6
4.8
5
radial distance r
×10^-7

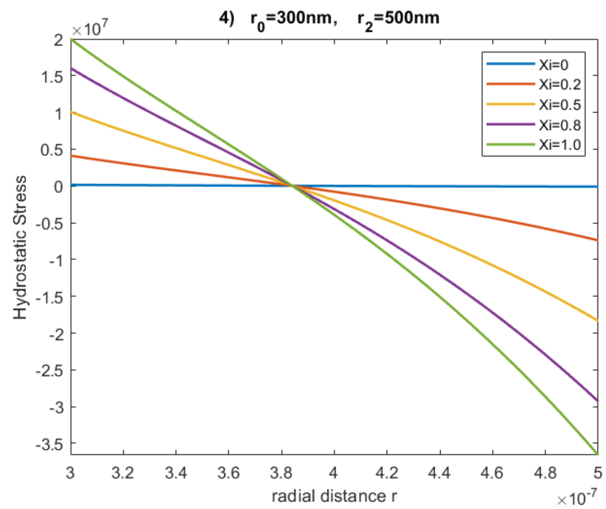
(a)


2) r0=300nm, r2=500nm
×10^7
1
0.5
0
-0.5
-1
-1.5
-2
Hydrostatic Stress
y=1
y=0
3
3.2
3.4
3.6
3.8
4
4.2
4.4
4.6
4.8
5
radial distance r
×10^-7

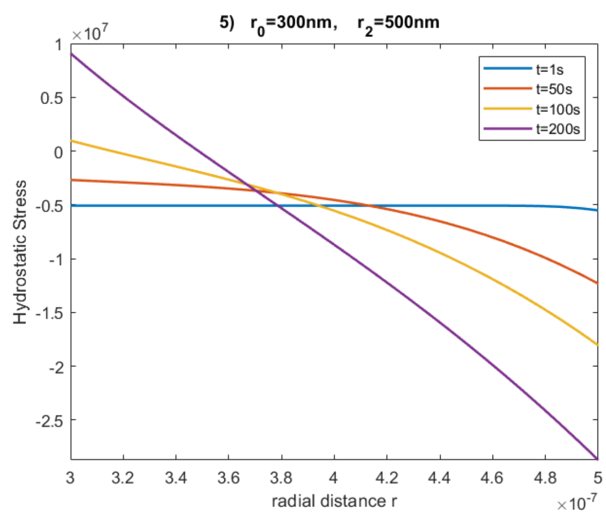
(b)


3) r0=300nm, r2=500nm
×10^7
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
Hydrostatic Stress
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
3
3.2
3.4
3.6
3.8
4
4.2
4.4
4.6
4.8
5
radial distance r
×10^-7

(c)

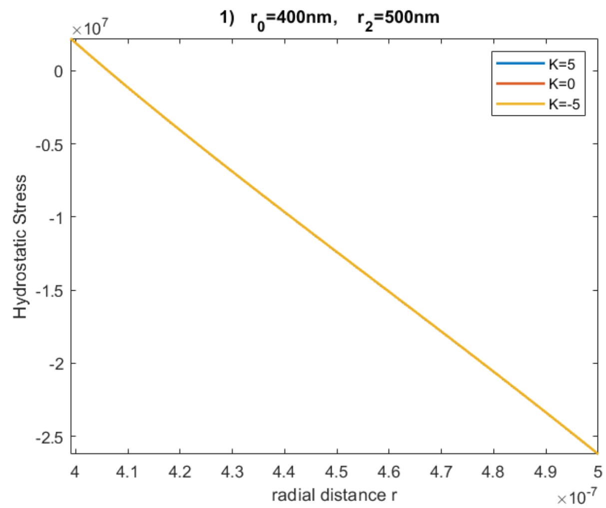


(d)

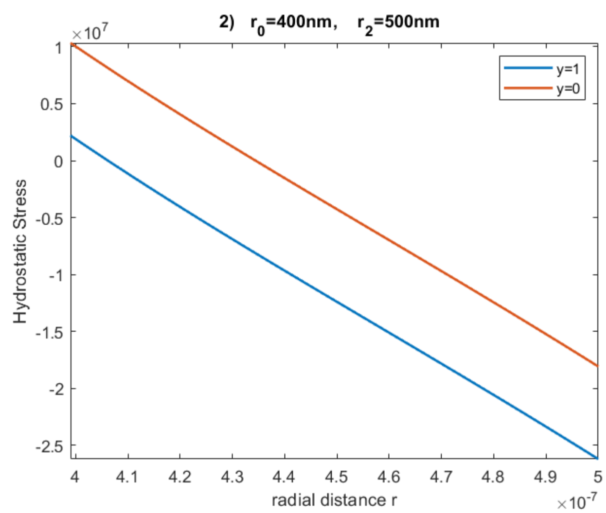


(e)

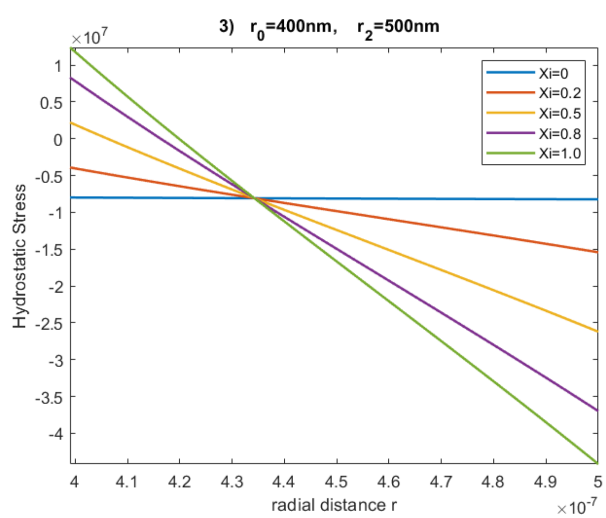
Figure 3.13: (a) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface modulus K, (b) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface energy γ, (c) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 1, (d) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 0, (e) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying time


1) r_0=400nm, r_2=500nm
×10^7
Hydrostatic Stress
radial distance r
×10^-7
K=5
K=0
K=-5

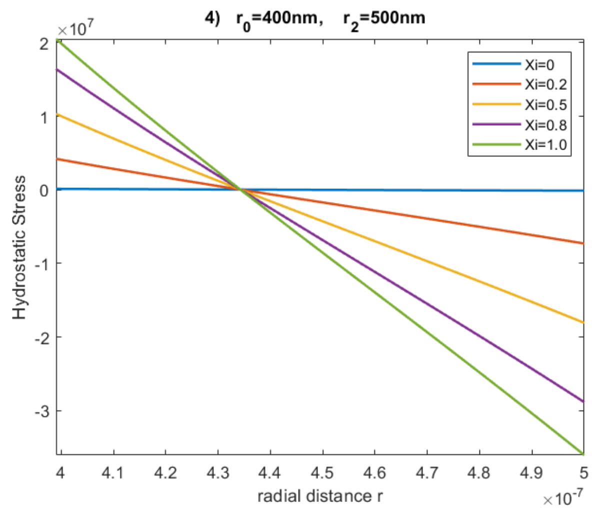
(a)


2) r_0=400nm, r_2=500nm
×10^7
Hydrostatic Stress
radial distance r
×10^-7
y=1
y=0

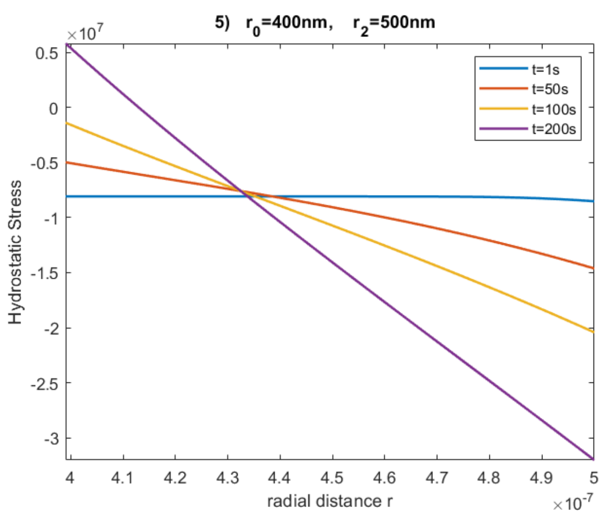
(b)


3) r_0=400nm, r_2=500nm
×10^7
Hydrostatic Stress
radial distance r
×10^-7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0

(c)

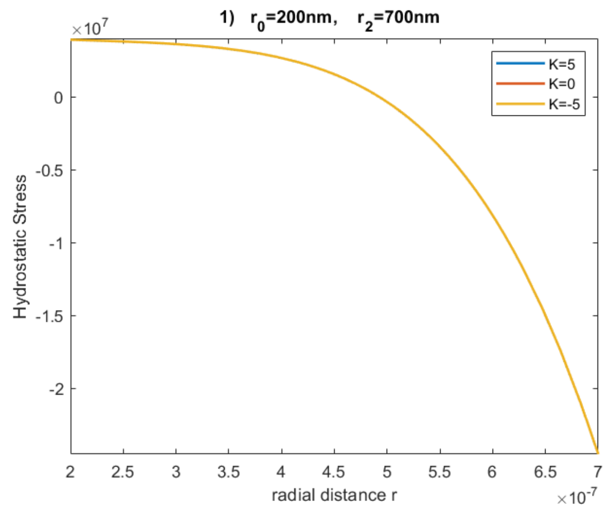


(d)

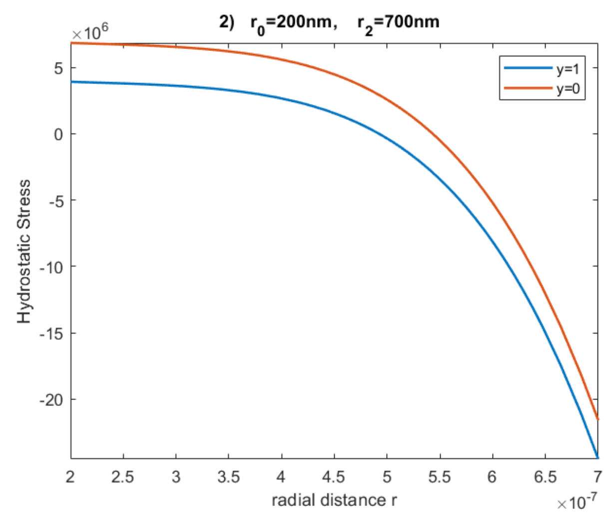


(e)

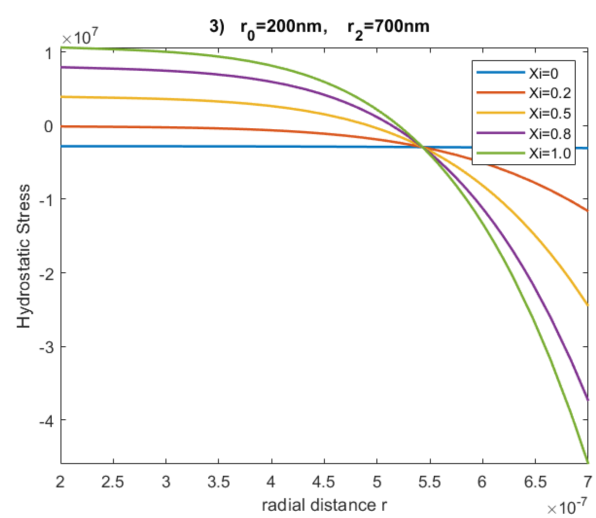
Figure 3.14: (a) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface modulus K, (b) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface energy γ, (c) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 1, (d) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 0, (e) Hydrostatic stress Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying time


1) r_0=200nm, r_2=700nm
$\times 10^7$
K=5
K=0
K=-5
Hydrostatic Stress
0
-0.5
-1
-1.5
-2
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
radial distance r
$\times 10^{-7}$

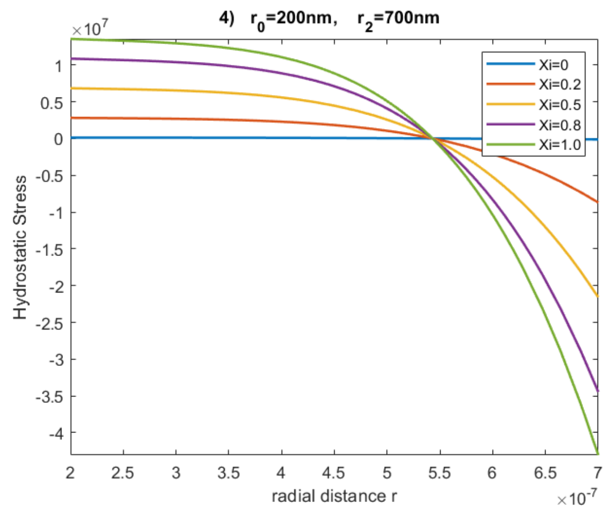
(a)


2) r_0=200nm, r_2=700nm
$\times 10^6$
y=1
y=0
Hydrostatic Stress
5
0
-5
-10
-15
-20
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
radial distance r
$\times 10^{-7}$

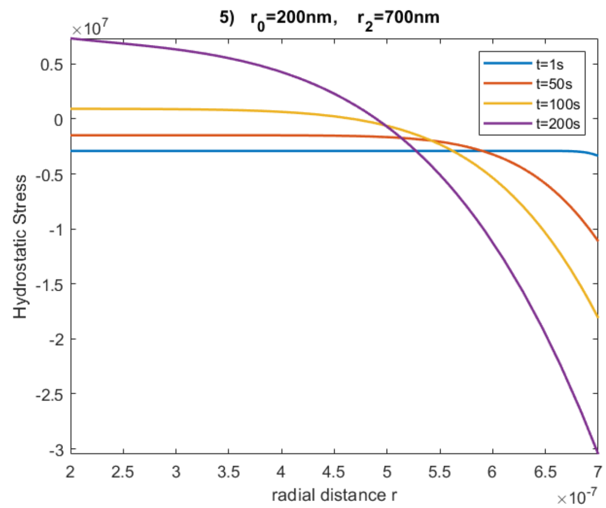
(b)


3) r_0=200nm, r_2=700nm
$\times 10^7$
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
Hydrostatic Stress
1
0
-1
-2
-3
-4
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
radial distance r
$\times 10^{-7}$

(c)

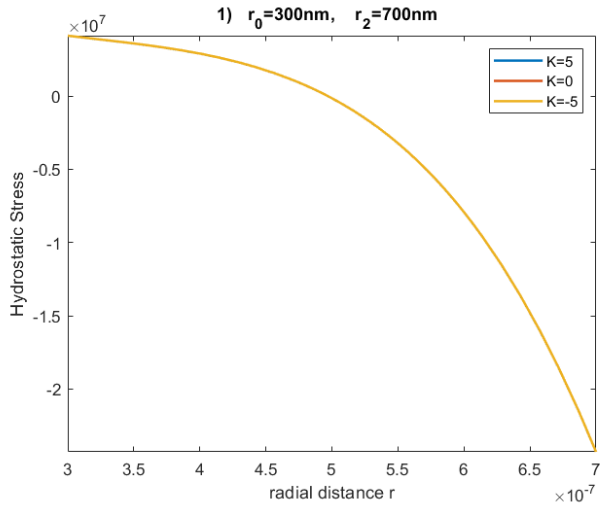


(d)

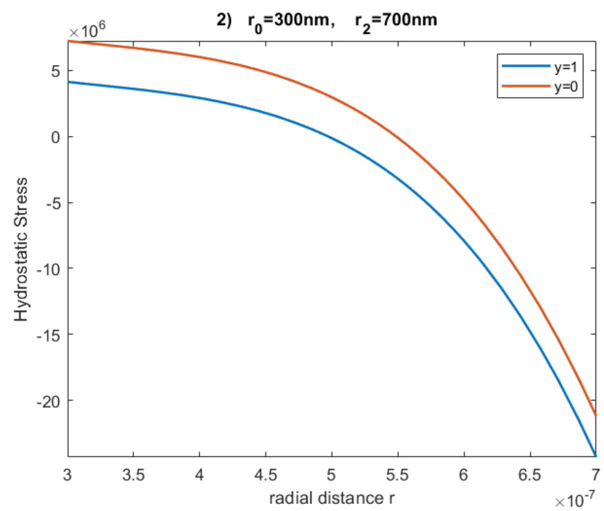


(e)

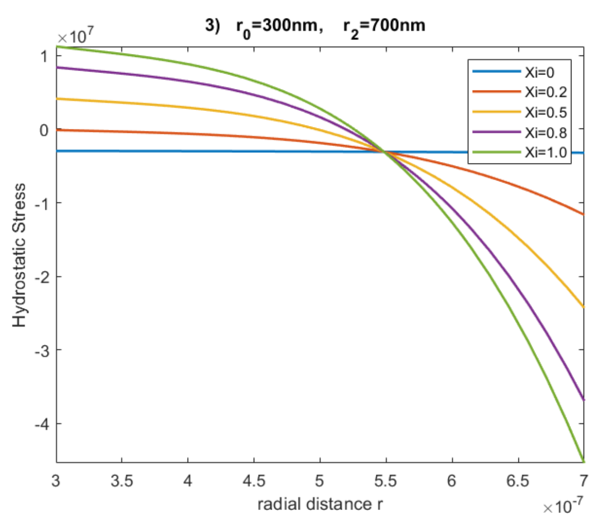
Figure 3.15: (a) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying surface modulus K, (b) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying surface energy γ, (c) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying ξ keeping γ equal to 1, (d) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying ξ keeping γ equal to 0, (e) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying time


1) r_0=300nm, r_2=700nm
×10^7
K=5
K=0
K=-5
Hydrostatic Stress
radial distance r
×10^-7

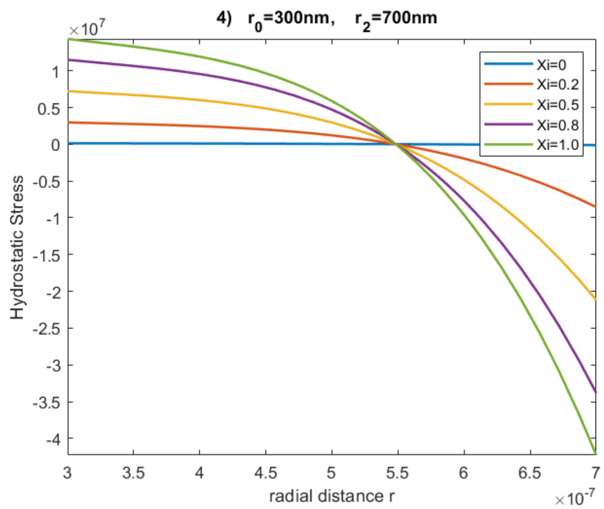
(a)


2) r_0=300nm, r_2=700nm
×10^6
y=1
y=0
Hydrostatic Stress
radial distance r
×10^-7

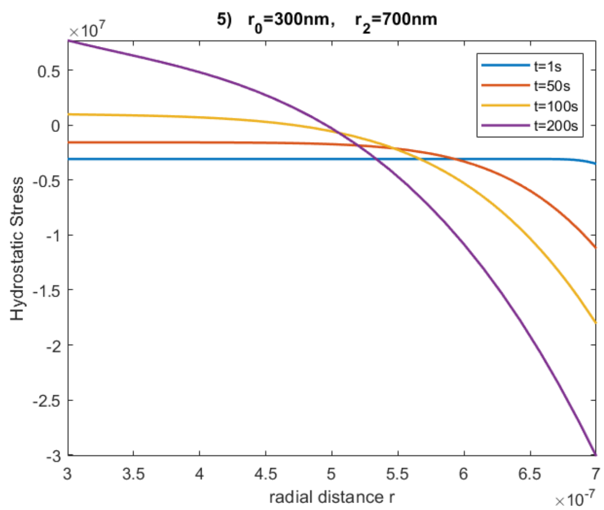
(b)


3) r_0=300nm, r_2=700nm
×10^7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
Hydrostatic Stress
radial distance r
×10^-7

(c)

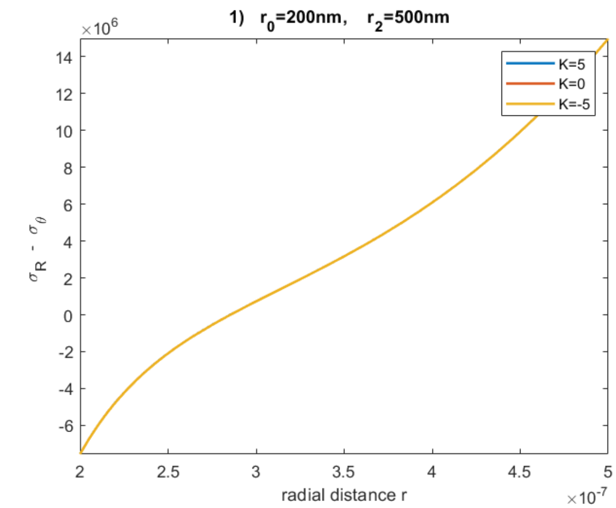


(d)

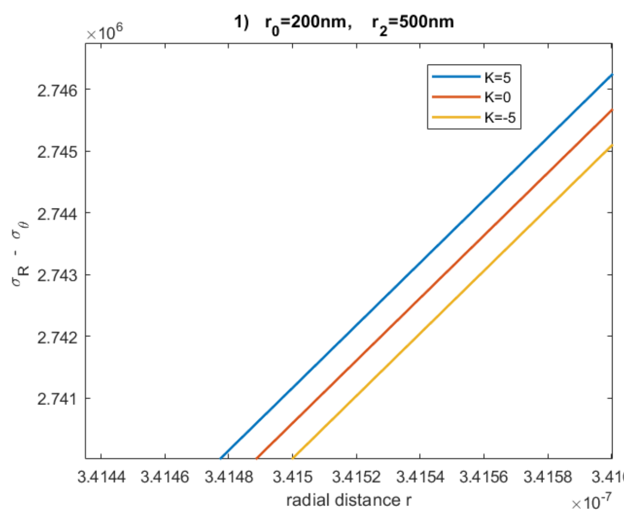


(e)

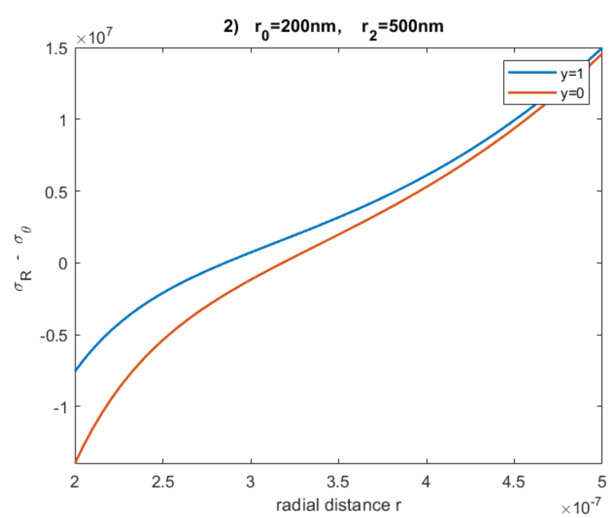
Figure 3.16: (a) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying surface modulus K, (b) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying surface energy γ, (c) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying ξ keeping γ equal to 1, (d) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying ξ keeping γ equal to 0, (e) Hydrostatic stress Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying time


1) r0=200nm, r2=500nm
×10^6
K=5
K=0
K=-5
σR - σθ
radial distance r
×10^-7

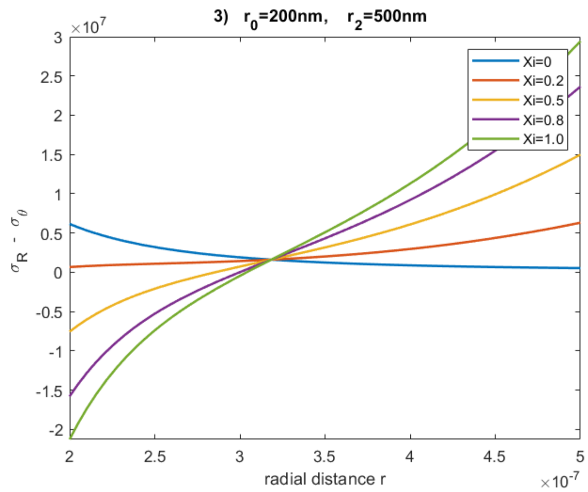
(a)


1) r0=200nm, r2=500nm
×10^6
K=5
K=0
K=-5
σR - σθ
radial distance r
×10^-7

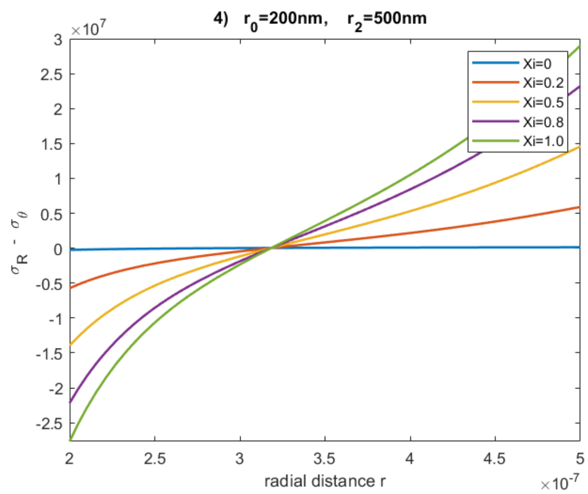
(b)


2) r0=200nm, r2=500nm
×10^7
y=1
y=0
σR - σθ
radial distance r
×10^-7

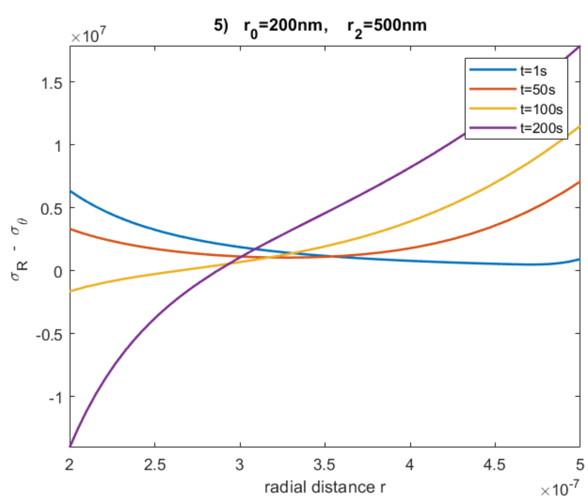
(c)



(d)

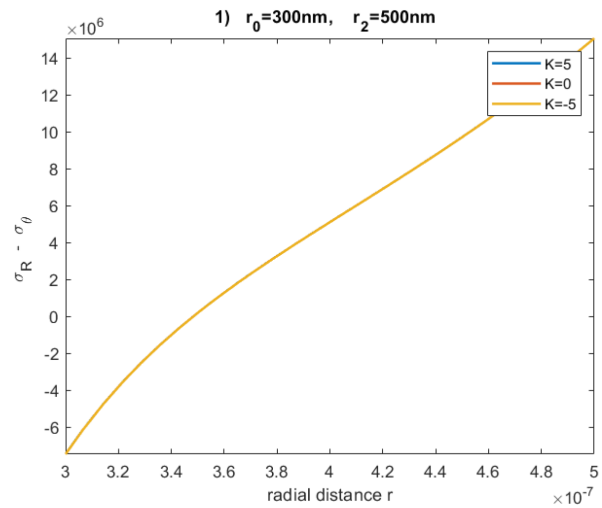


(e)



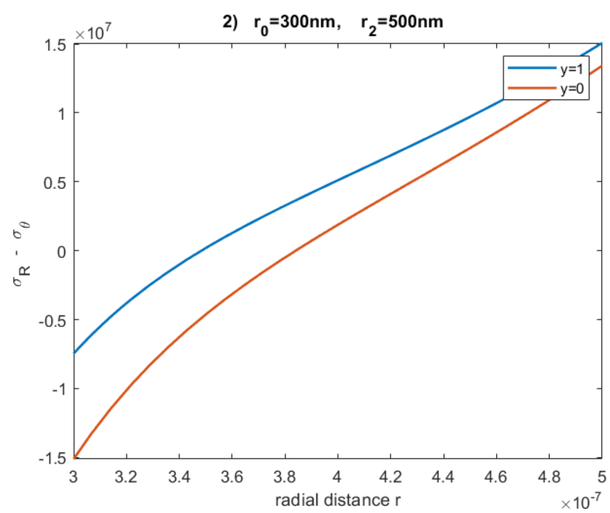
(f)

Figure 3.17: (a) $\sigma_r\,(r,t)-\sigma_\theta\,(r,t)$ Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying surface modulus K, (b) Distinguishing $\sigma_r\,(r,t)-\sigma_\theta\,(r,t)$ with different values of surface modulus K, (c) $\sigma_r\,(r,t)-\sigma_\theta\,(r,t)$ Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying surface energy γ, (d) $\sigma_r\,(r,t)-\sigma_\theta\,(r,t)$ Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying ξ keeping γ equal to 1, (e) $\sigma_r\,(r,t)-\sigma_\theta\,(r,t)$ Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying ξ keeping γ equal to 0, (f) $\sigma_r\,(r,t)-\sigma_\theta\,(r,t)$ Vs Radial distance (r_2=500 nm, r_0=200 nm) with varying time



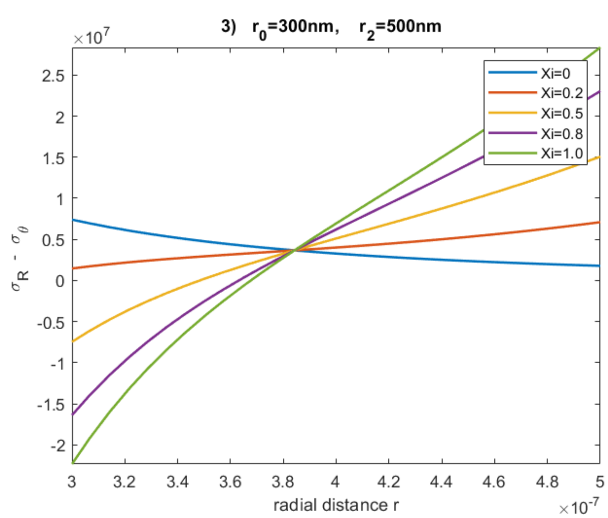
1) r_0=300nm, r_2=500nm
×10^6
K=5
K=0
K=-5
σ_R - σ_θ
radial distance r
×10^-7

(a)



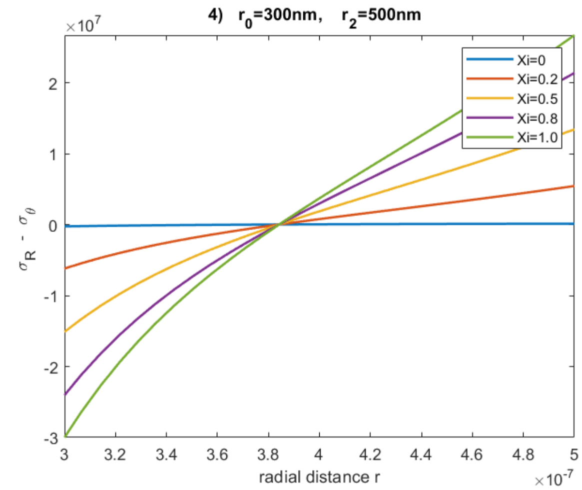
2) r_0=300nm, r_2=500nm
×10^7
y=1
y=0
σ_R - σ_θ
radial distance r
×10^-7

(b)

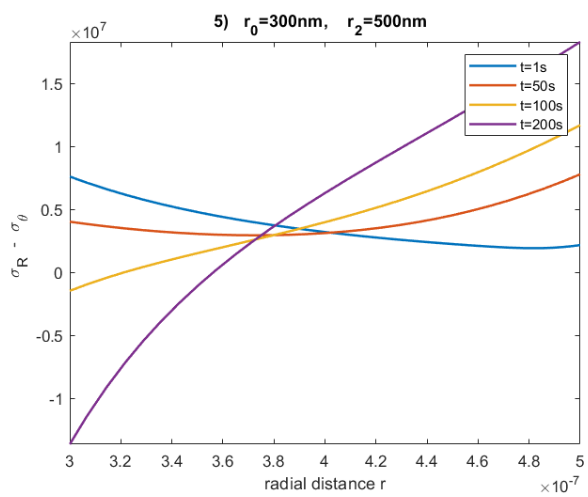


3) r_0=300nm, r_2=500nm
×10^7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
σ_R - σ_θ
radial distance r
×10^-7

(c)

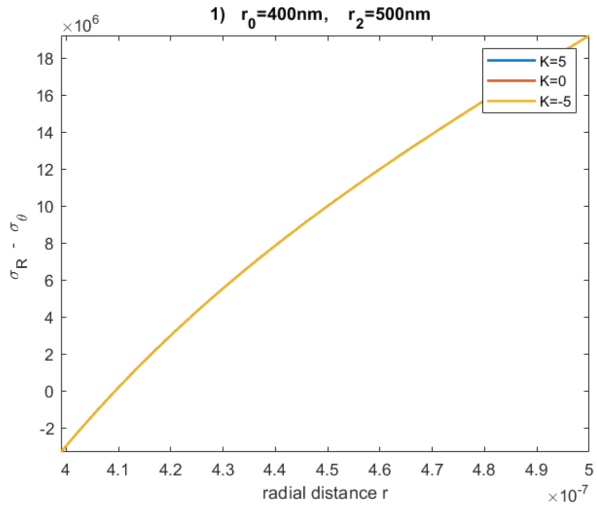


(d)

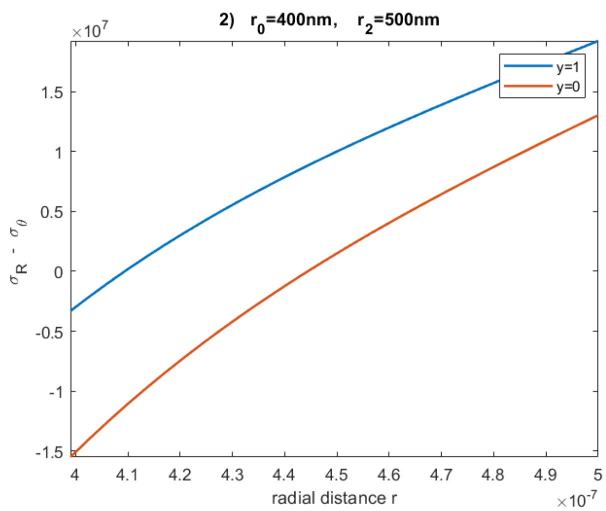


(e)

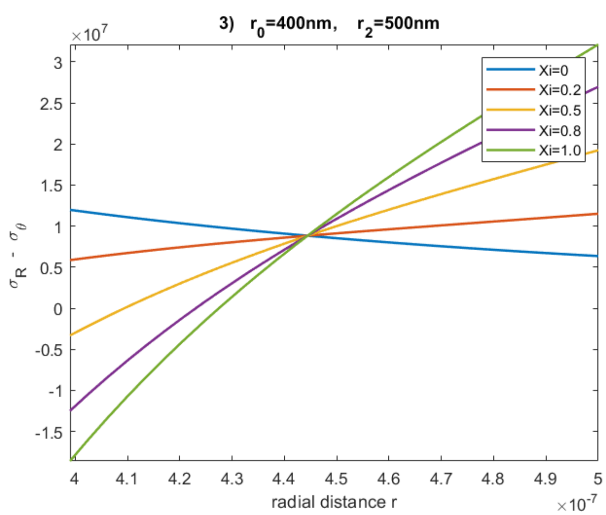
Figure 3.18: (a) $\sigma_r(r,t)-\sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface modulus K, (b) $\sigma_r(r,t)-\sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying surface energy γ, (c)$\sigma_r(r,t)-\sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 1, (d) $\sigma_r(r,t)-\sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying ξ keeping γ equal to 0, (e) $\sigma_r(r,t)-\sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=300 nm) with varying time


1) r0=400nm, r2=500nm
×10^6
K=5
K=0
K=-5
σR - σθ
radial distance r
×10^-7

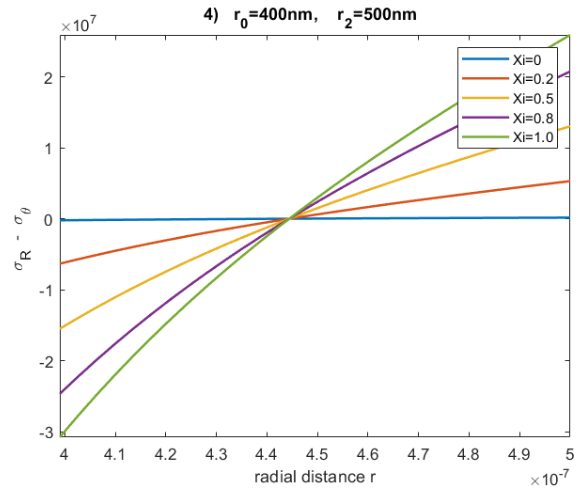
(a)


2) r0=400nm, r2=500nm
×10^7
y=1
y=0
σR - σθ
radial distance r
×10^-7

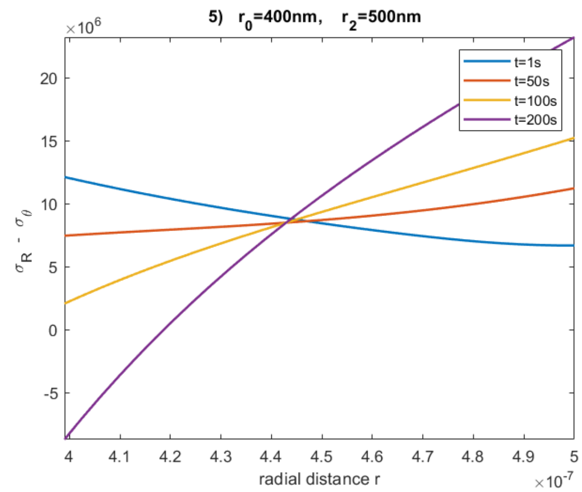
(b)


3) r0=400nm, r2=500nm
×10^7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
σR - σθ
radial distance r
×10^-7

(c)

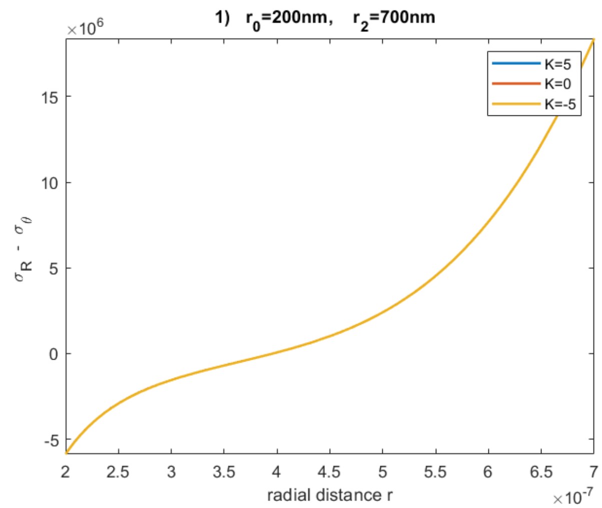


(d)

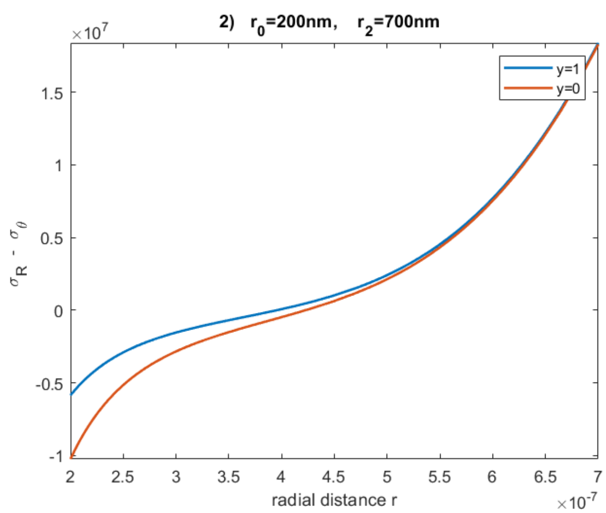


(e)

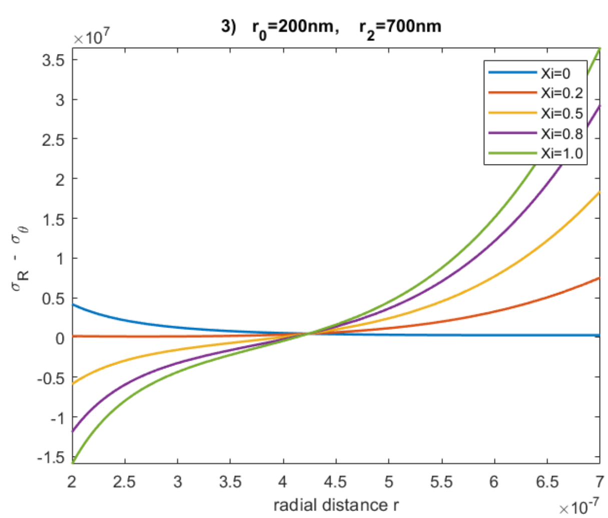
Figure 3.19: (a) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying surface modulus K, (b) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying surface energy γ, (c) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying ξ keeping γ equal to 1, (d) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying ξ keeping γ equal to 0, (e) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=500 nm, r_0=400 nm) with varying time


1) r_0=200nm, r_2=700nm
$\times 10^6$
K=5
K=0
K=-5
15
10
5
0
-5
σ_R - σ_θ
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
radial distance r
$\times 10^{-7}$

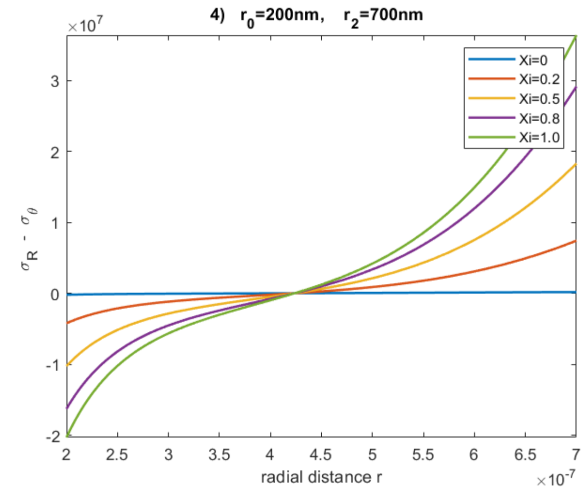
(a)


2) r_0=200nm, r_2=700nm
$\times 10^7$
y=1
y=0
1.5
1
0.5
0
-0.5
-1
σ_R - σ_θ
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
radial distance r
$\times 10^{-7}$

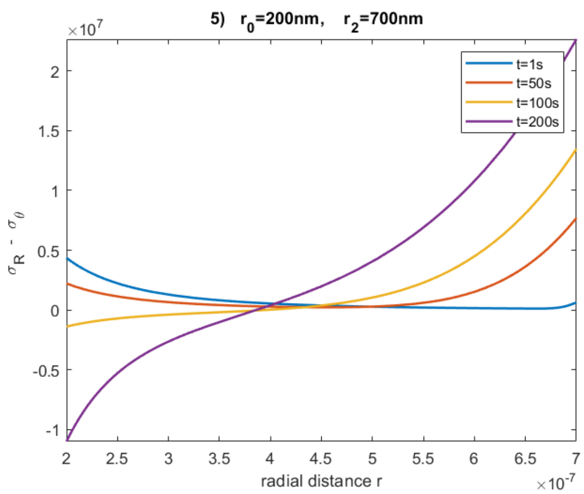
(b)


3) r_0=200nm, r_2=700nm
$\times 10^7$
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
σ_R - σ_θ
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
radial distance r
$\times 10^{-7}$

(c)

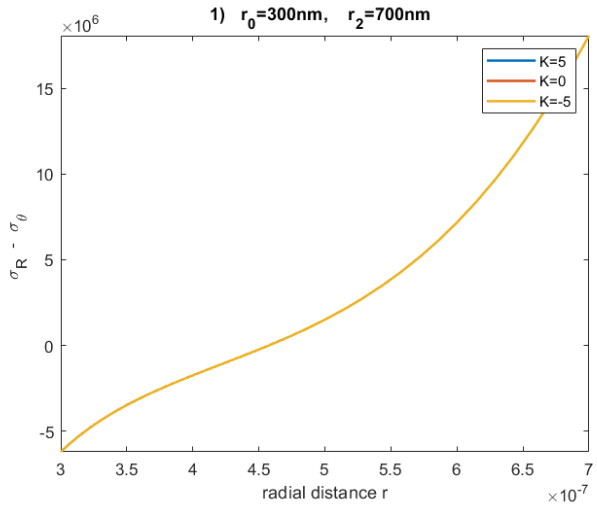


(d)

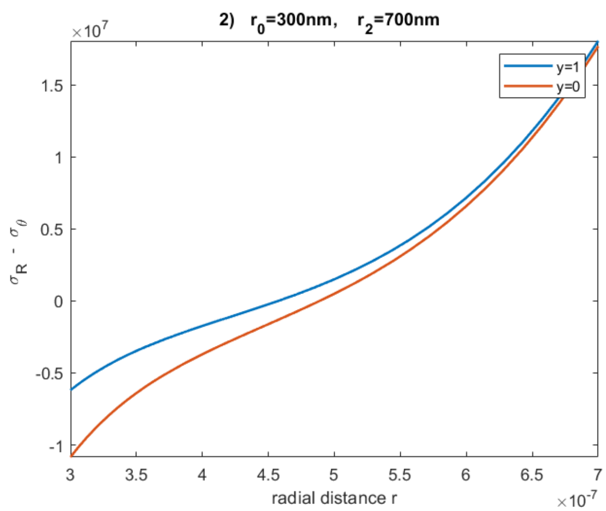


(e)

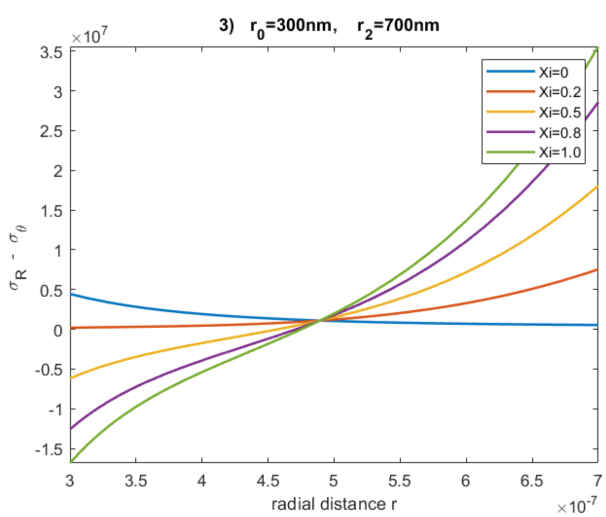
Figure 3.20: (a) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying surface modulus K, (b) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying surface energy γ, (c) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying ξ keeping γ equal to 1, (d) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying ξ keeping γ equal to 0, (e) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=200 nm) with varying time


1) r0=300nm, r2=700nm
×10^6
K=5
K=0
K=-5
15
10
5
0
-5
σR - σθ
3
3.5
4
4.5
5
5.5
6
6.5
7
radial distance r
×10^-7

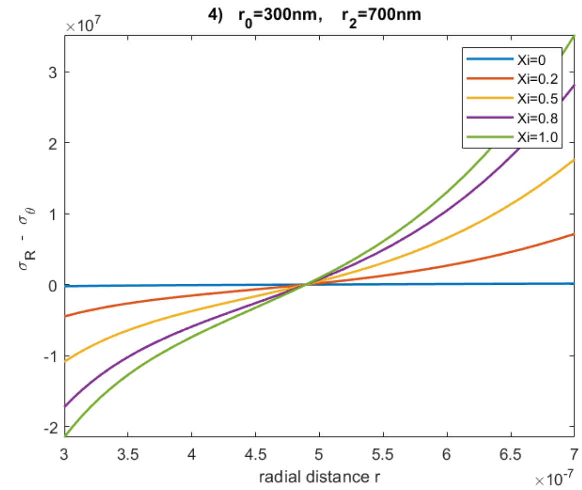
(a)


2) r0=300nm, r2=700nm
×10^7
y=1
y=0
1.5
1
0.5
0
-0.5
-1
σR - σθ
3
3.5
4
4.5
5
5.5
6
6.5
7
radial distance r
×10^-7

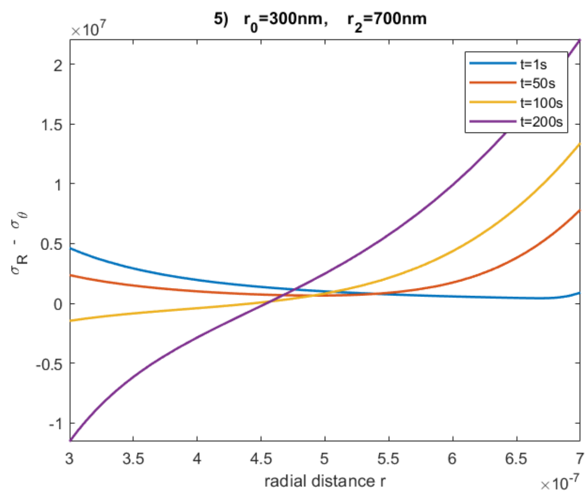
(b)


3) r0=300nm, r2=700nm
×10^7
Xi=0
Xi=0.2
Xi=0.5
Xi=0.8
Xi=1.0
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
σR - σθ
3
3.5
4
4.5
5
5.5
6
6.5
7
radial distance r
×10^-7

(c)



(d)



(e)

Figure 3.21: (a) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying surface modulus K, (b) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying surface energy γ, (c) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying ξ keeping γ equal to 1, (d) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying ξ keeping γ equal to 0, (e) $\sigma_r(r,t) - \sigma_\theta(r,t)$ Vs Radial distance (r_2=700 nm, r_0=300 nm) with varying time

Table 3.1: Values of material properties and parameter used in the simulation

Sr.No	**Symbol**	**Material property or parameter**	**Values**
1	E	Young's modulus of pure Silicon	90.13 GPa [51]
2	v	Poisson's ratio of Silicon	0.28 [37]
3	Ω	Partial molar volume of lithium	9 x $10^{-6} m^3 mol^{-1}$ [52]
4	X_{max}	Maximum saturation of lithium in Li_xSi_y	4.4 [47]
5	η_E	Rate of change of elastic modulus with concentration	- 0.1464 [37] [47] [51]
6	σ_γ	Initial yield stress of Silicon	0.12 GPa [53]
7	D	Diffusivity of lithium in silicon	1 x $10^{-16} m^2 s^{-1}$ [29][28]
8	K	Surface modulus	- 5, + 5 Nm^{-1} [54]
9	γ	Surface energy	1 Jm^{-2} [54]
10	τ_{rs}	Deformation independent residual stress	0 [42]
11	C_1	Li (Conc.) at the inner surface	0
12	C_2	Li (Conc.) at the outer surface	1 $molm^{-3}$
13	β	Volumetric swelling ratio for silicon	4 [55]
14	$f(r)$	Initial concentration function	0
15	ξ	Parametric constant	0-1 [34]
16	ε	Linear function coefficients for concentration	1.4 x 10^{-7} $GPa\ mol^{-1} m^3$ [54]