COMSOL phase field fatigue model for battery materials

Weilong Ai[a,b,c], Emilio Martínez-Pañeda[d,*]

[a]*School of Civil Engineering, Southeast University, Nanjing, China*
[b]*Dyson School of Design Engineering, Imperial College London, London SW7 2AZ, UK*
[c]*The Faraday Institution, Quad One, Becquerel Avenue, Harwell Campus, Didcot, OX11 0RA, UK*
[d]*Department of Civil and Environmental Engineering, Imperial College London, London SW7 2AZ, UK*

Abstract

Documentation that accompanies the `COMSOL` implementation of a phase field coupled deformation-diffusion-fracture/fatigue model for predicting cracking in electrode particles of Li-Ion batteries. The code can be downloaded from `www.empaneda.com/codes`. If using these codes for research or industrial purposes, please cite the following article:

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1. Preliminaries

The phase field fracture model has gained remarkable popularity for its ability to robustly capture complex phenomena in a physically sound manner, based on Griffith and the thermodynamics of fracture [1]. Phase field models are also well-suited for multi-physics problems, as the phase field evolution equation can readily be coupled to equations describing other physical phenomena. As such, coupled deformation-diffusion-fracture schemes based on the phase field model have been developed for multi-physics problems such as hydrogen embrittlement [2–5], stress corrosion cracking [6, 7] and Li-Ion batteries [8–10]. Here, we present a `COMSOL` implementation of a coupled deformation-diffusion-fracture phase field model capable of predicting the evolution of static and fatigue cracks in electrode particles and other Li-Ion battery materials.

We take advantage of `COMSOL`'s in-built symbolic differentiation features, implying that we only need to introduce the strong form equation. Our primal variables are the displacement field $\mathbf{u}$, the concentration of diluted species c and the phase field fracture parameter ϕ. These are solved as degrees-of-freedom by solving the following three local balance equations for linear momentum,

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*Corresponding author.
Email address:* `e.martinez-paneda@imperial.ac.uk` (Emilio Martínez-Pañeda)

Fickian diffusion and phase field fatigue crack, respectively:

$$[(1 - \phi)^2 + k]\boldsymbol{\nabla} \cdot \boldsymbol{\sigma} = 0 \tag{1a}$$

$$\frac{\partial c}{\partial t} = \boldsymbol{\nabla} \cdot (D\boldsymbol{\nabla}c - \frac{\Omega c}{RT}\boldsymbol{\nabla}\sigma_h) \tag{1b}$$

$$G_d\frac{\phi}{l_0} - l_0\Delta(G_d\phi) - 2(1 - \phi)\psi^+(\boldsymbol{\varepsilon}) = 0 \tag{1c}$$

These equations have primal field variables (the unknowns), parameters (constants) and variables that are a function of the primal variables.

In this case, the parameters that we need are:

- Linear elastic properties: E and ν

- Diffusion coefficient: D

- Partial molar volume: Ω

- Gas constant: R

- Temperature: T

- Critical energy release rate (toughness): G_c

- Phase field length scale: l_0

- Numerical parameter for stability: k

- Fatigue crack threshold: $\alpha_T = \frac{G_c}{12l}$

And we will define the following variables:

- Degradation function: $g(\phi) = [(1 - \phi)^2 + k]$

- Hydrostatic stress: σ_h

- Active part of strain energy density: $\psi^+(\boldsymbol{\varepsilon})$

- Historic variable: $\alpha = g(\phi)\psi^+(\boldsymbol{\varepsilon})$

- Cumulative historic variable: $\bar{\alpha} = \int_0^t H(\alpha\dot{\alpha})|\dot{\alpha}|d\tau$

- Fatigue historic variable: $\alpha = \psi^+(\boldsymbol{\varepsilon})$

- Fatigue degradation function: $f(\bar{\alpha}) = \begin{cases} 1 & \text{if} \quad \bar{\alpha} \leq \alpha_T \\[2mm] \frac{2\alpha_T}{\bar{\alpha}+\alpha_T} & \text{if} \quad \bar{\alpha} > \alpha_T \end{cases}$

- Degraded fracture toughness: $G_d = f(\bar{\alpha})G_c$

2. COMSOL implementation

Let's start by choosing a simple 3D model: a sphere with one ring crack subjected to a flux loading on the surface (with axisymmetric assumptions) – see Fig. 1 below.
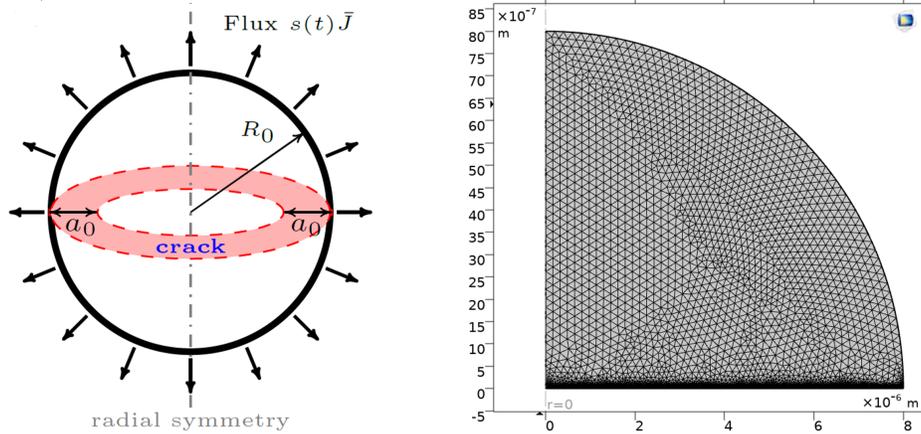

Figure 1: The geometry of a spherical particle with a ring crack.

We use the Model Wizard to select 2D axisymmetric and the following physics nodes: (1) Solid Mechanics [Structural Mechanics group], (2) Transport of Diluted Species [Chemical species transport group], (3) Helmholtz equation [Classical PDEs, Mathematics group]. As a first step we define the parameters of the model as blow, following the list given above and noting that the gas constant is in-built in `COMSOL` as "R_const".

2.1. Solid Mechanics

First, note that in the Solid Mechanics settings we can choose to define the Structural Transient Behavior as "Quasi-static" or "Include inertial terms". In the Linear Elastic Material Settings we define as Young's modulus the variable Eg, which is a multiplication of Young's modulus by the degradation function. We then make also user defined Poisson's ratio and density, making them equal to the parameters that we have defined (nu and rho, respectively). Then, we incorporate

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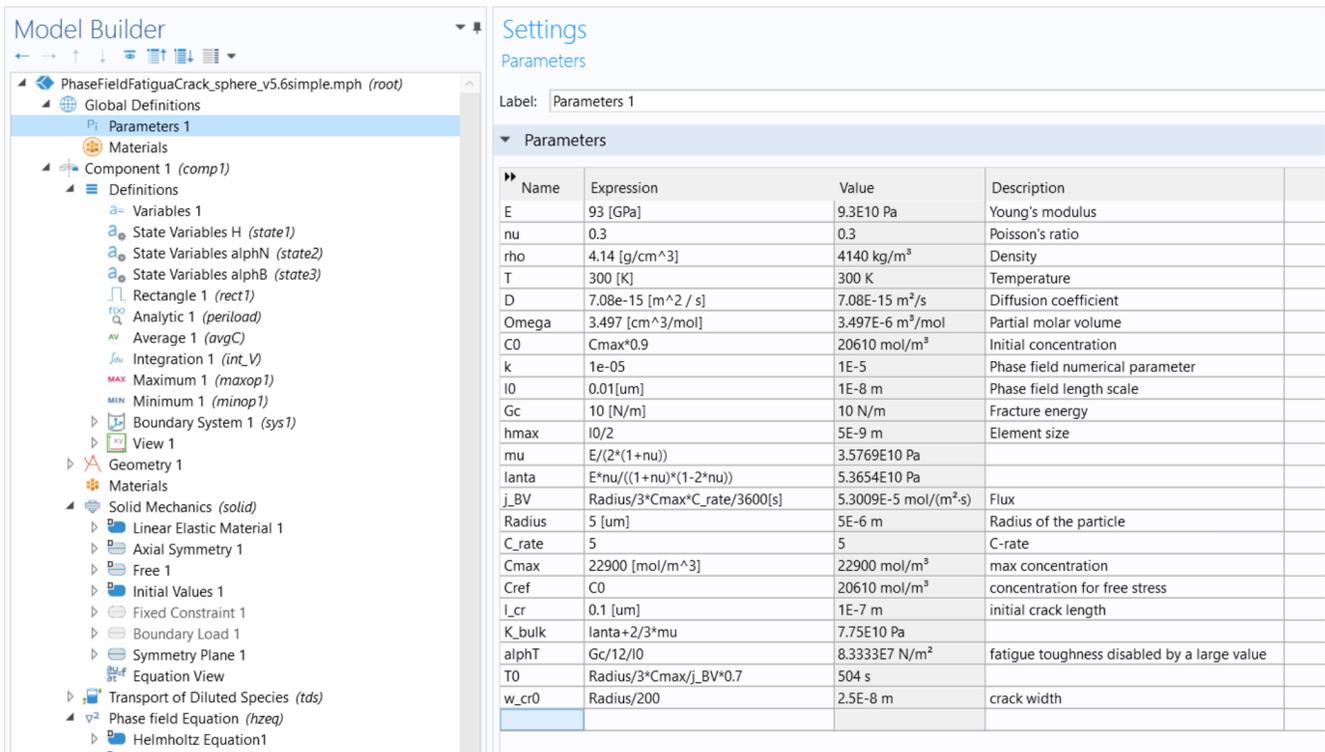
Figure 2: List of parameters of the model.

Name	Expression	Value	Description
E	93 [GPa]	9.3E10 Pa	Young's modulus
nu	0.3	0.3	Poisson's ratio
rho	4.14 [g/cm^3]	4140 kg/m³	Density
T	300 [K]	300 K	Temperature
D	7.08e-15 [m^2 / s]	7.08E-15 m²/s	Diffusion coefficient
Omega	3.497 [cm^3/mol]	3.497E-6 m³/mol	Partial molar volume
C0	Cmax*0.9	20610 mol/m³	Initial concentration
k	1e-05	1E-5	Phase field numerical parameter
l0	0.01[um]	1E-8 m	Phase field length scale
Gc	10 [N/m]	10 N/m	Fracture energy
hmax	l0/2	5E-9 m	Element size
mu	E/(2*(1+nu))	3.5769E10 Pa	
lanta	E*nu/((1+nu)*(1-2*nu))	5.3654E10 Pa	
j_BV	Radius/3*Cmax*C_rate/3600[s]	5.3009E-5 mol/(m²·s)	Flux
Radius	5 [um]	5E-6 m	Radius of the particle
C_rate	5	5	C-rate
Cmax	22900 [mol/m^3]	22900 mol/m³	max concentration
Cref	C0	20610 mol/m³	concentration for free stress
l_cr	0.1 [um]	1E-7 m	initial crack length
K_bulk	lanta+2/3*mu	7.75E10 Pa	
alphT	Gc/12/l0	8.3333E7 N/m²	fatigue toughness disabled by a large value
T0	Radius/3*Cmax/j_BV*0.7	504 s	
w_cr0	Radius/200	2.5E-8 m	crack width

the role of chemical strains by taking advantage of the analogy with hygroscopic swelling. Thus, we add a Hygroscopic Swelling subnode under the Linear Elastic Material node. The equation is the usual one, as shown in fig. 8.
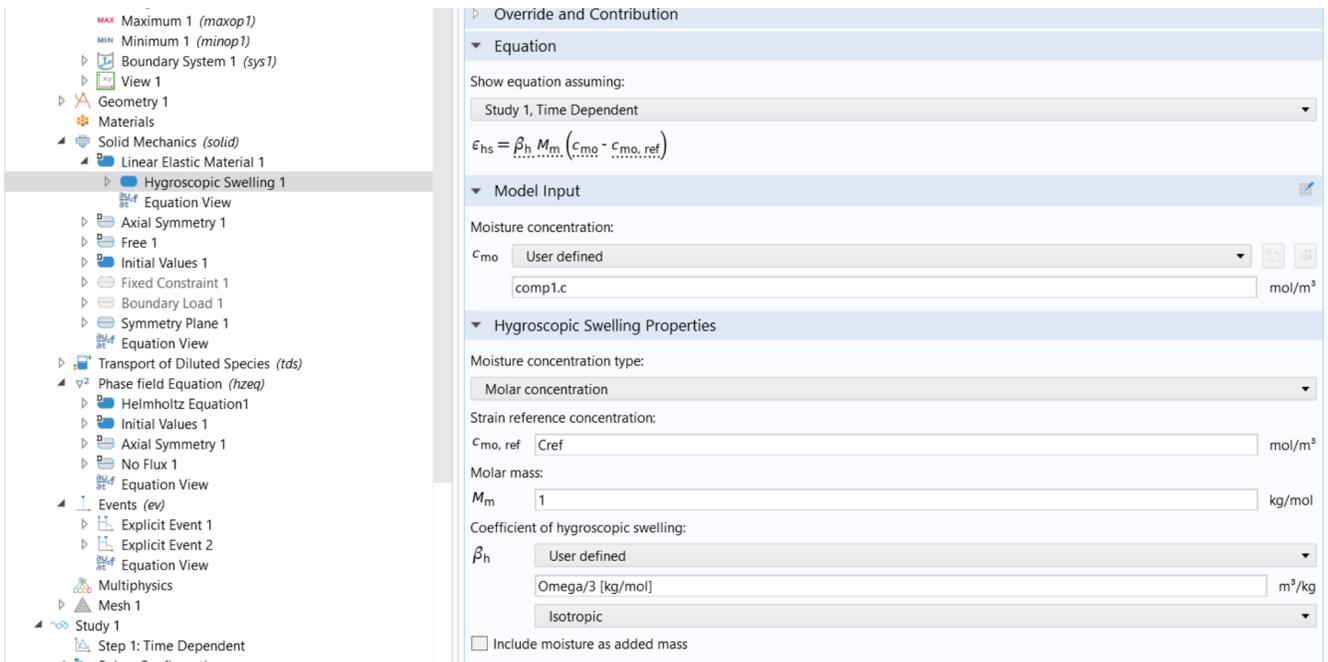
Figure 3: Inputs for the hygroscopic swelling strain.

This equation agrees with the chemical strains expression:

$$\boldsymbol{\varepsilon}^{\text{ch}} = \frac{\Omega}{3}(c - c_{ref})\mathbf{I} \tag{2}$$

Use the following setups:

- moisture concentration c_{mo} as user defined: "comp1.c"

- moisture concentration type: "molar concentration"

- strain reference concentration $c_{mo,ref}$: "Cref"

- molar mass: "1"

- coefficient of hygroscopic swelling β_h: "Omega/3 [kg/mol]"

It is also important to define symmetry boundary conditions, using the subnode of Symmetry Plane and choosing the right boundary lines. For the hydrostatic stress, the simplest option is to define it from the internal value for pressure: "Sh = - solid.pm". Regarding the historic field "H", it is defined in the state field, using "H=if(fai_p>H, fai_p, H)", where the if operator follows the order (True,False). Here, fai_p (ψ^+) is the tensile strain energy and follows the definition of the so-called volumetric-deviatoric split [11]:

$$\psi_0^+ = 0.5K \left\langle \text{tr}\left(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_{Li}\right)\right\rangle_+^2 + \mu \left(\boldsymbol{\varepsilon}^{\text{dev}} : \boldsymbol{\varepsilon}^{\text{dev}}\right) \tag{3a}$$

$$\psi_0^- = 0.5K \left\langle \text{tr}\left(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_{Li}\right)\right\rangle_-^2 \tag{3b}$$

where K is the bulk modulus, $\boldsymbol{\varepsilon}^{\text{dev}}$ is the deviatoric elastic strain, i.e. $\boldsymbol{\varepsilon}^{\text{dev}} = (\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_{\text{Li}}) - \text{tr}(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_{\text{Li}})\mathbf{I}/3$ and the operator $\langle \cdot \rangle_\pm = (x \pm |x|)/2$.

2.2. Transport of diluted species

First, we define as additional transport mechanism "Convection", which will lead to an equation of the type:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i + \mathbf{u}c_i) = R_i \tag{4a}$$

$$\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u}c_i \tag{4b}$$
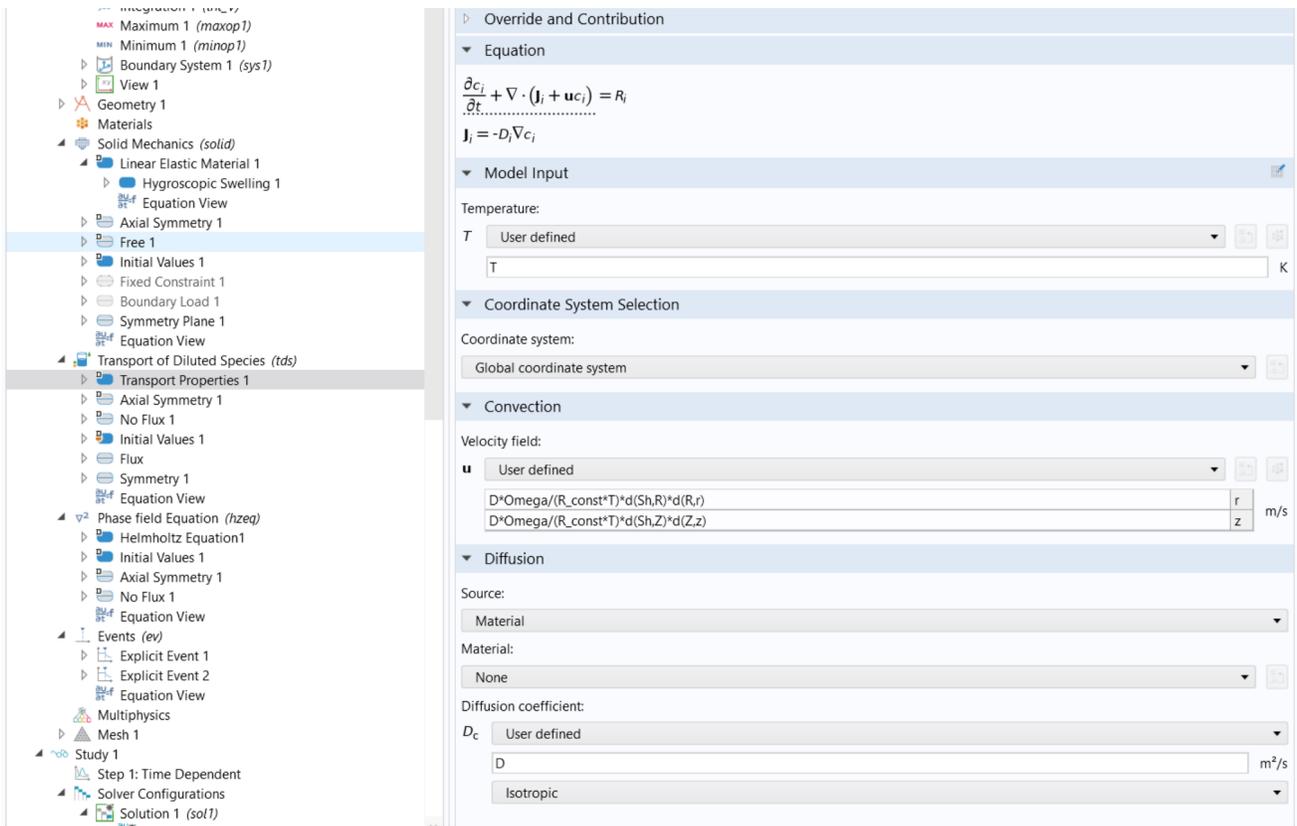
Figure 4: Inputs for the transport of diluted species.

The transport of diluted species is defined as shown in Fig. 4.

From Eq. (1b), it implies that $R_i = 0$, and:

- ux: "D*Omega/(R_const*T)*d(Sh,R)*d(R,r)"

- uy: "D*Omega/(R_const*T)*d(Sh,Z)*d(Z,z)"

where "R, Z" and "r, z" are for the material and spatial frames, respectively. For newer versions than COMSOL 5.6, there are issues with the "laginterpdiff" function for derivatives of Sh in spatial frame (see COMSOL/failed-to-evaluate-jacobian-of-operator), while there is no problem with the derivatives in material frame, so the chain rule is used to obtain the derivatives of Sh in spatial frame. We define as user defined temperature as parameter T and diffusion coefficient as D. In addition, we introduce as initial values c: "C0". For flux boundary conditions, a periodic fluxing loading is defined using "periload(t)*j_BV", where "periload(t)" is a modified sign function to switch between charge and discharge. One event is defined at t=n*T0 to avoid the solver skipping these switching times.
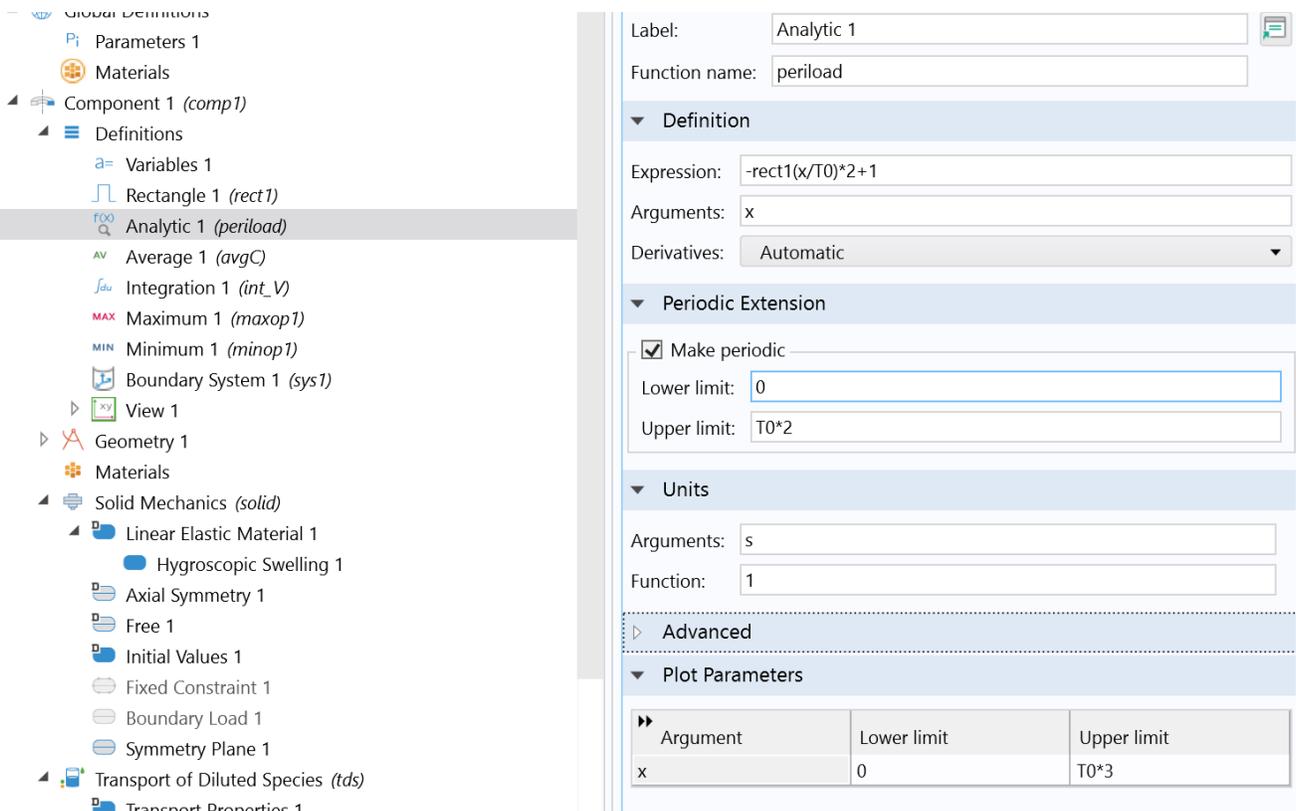
Figure 5: Periodic function for cycling.

2.3. Helmholtz Equation (Phase field)

We name the dependent variable "p" and make the quantity (and the source term) dimensionless. The equation is of the form:
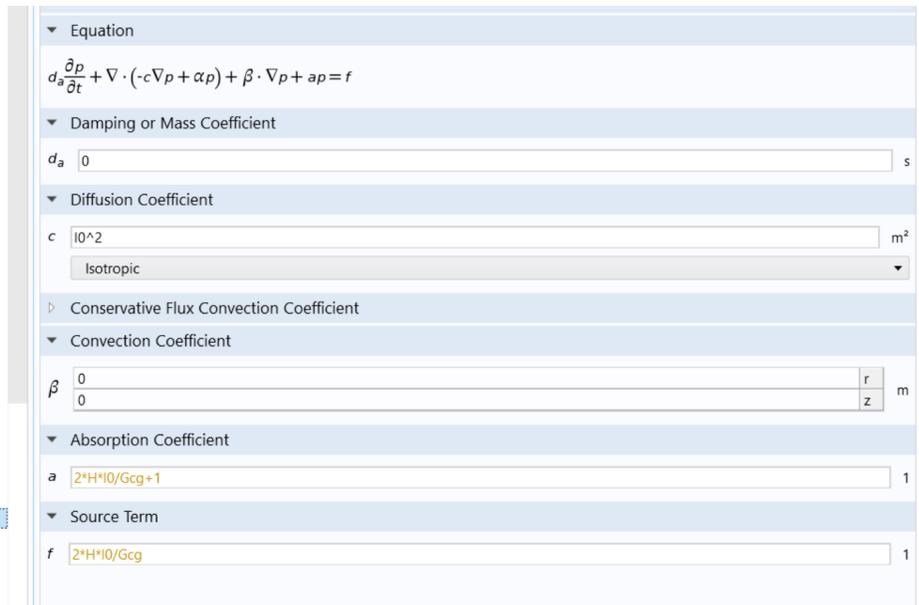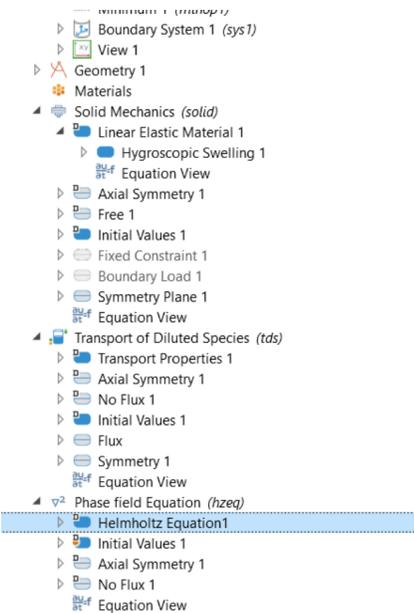

Figure 6: The phase field crack model.

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Accordingly, eq. (1c) results in the following weak form equation:

$$\int_{\partial\Omega} \mathbf{n} \cdot (-c\nabla p\delta p)\mathrm{dS} + \int_{\Omega} (c\nabla p) \cdot \nabla\delta p\mathrm{d}\Omega + \int_{\Omega} \{ap - f\}\delta p\mathrm{d}\Omega = 0 \tag{5}$$

It implies that we can define in `COMSOL`:

- Diffusion coefficient c: "l0*l0"

- Source term f: "2*H*l0/Gd"

- Absorption coefficient a: "2*H*l0/Gd+1"

No extra boundary condition is defined, except the default one. If an initial crack exists, in phase field fracture the crack can be defined by prescribing p in the Helmholtz Equation or by prescribing a high value for H.


Figure 7: State variables for the fatigue crack model.

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2.4. Fatigue crack

For fatigue crack models, an important step to calculate $\bar{\alpha}$, an input for the fatigue degradation function. We use a discrete approach to integrate over time for $\bar{\alpha}$ using: "alphB=if(alph*(alph-alphN)>0, alphB+abs(alph-alphN), alphB)". These two variables of alphaN and alphaBN are defined with state variables.

2.5. Mesh

We then move on to meshing. First, by clicking in the eye on the top of the Model Tree we enable seeing the Discretization settings. For Solid Mechanics we use "Cubic Lagrange", for Transport of Diluted Species we use "Quadratic", and for Helmholtz Equation we go for "Quadratic". Regarding the specific mesh. We edit the Size subnode and use General Physics, and predefined as "custom". And then we create a subsubnode Size where we specify as minimum element size the parameter hmax.
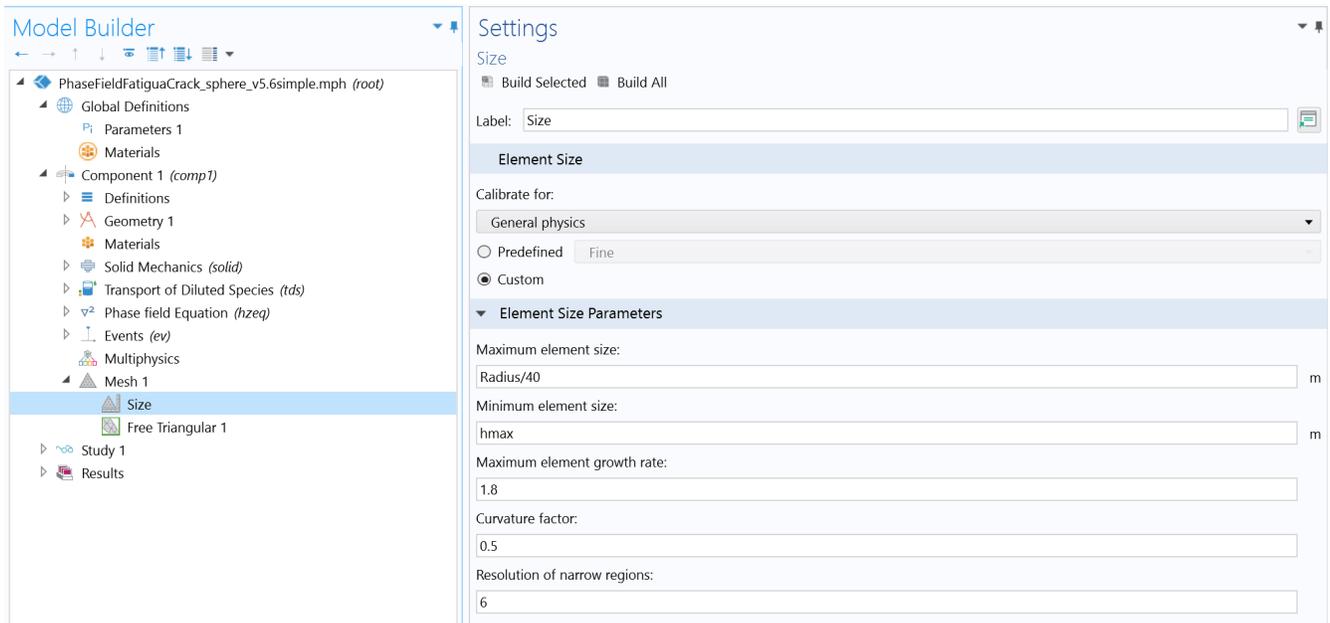

Figure 8: Mesh and element size.

2.6. Solver

The one-before-last step involves defining the solver features. First, we define the times. Which is a range from 0 to 2*n*T0 and we must define a sufficient number of increments. One should be careful when choosing the cycle number n, where a large value will make the simulation time-consuming.

We do not include geometric nonlinearity as we are not dealing with large strains. And we will later select what plot group we want to show while solving. The same steps have to be done in the Time Dependent Solver 1 subnode: define the appropriate range and plot the phase field. Many other Step options are available and should be explored if convergence problems arise.

As we have discussed before, we need to define, within the Time Dependent Solver node, a subnode of the type "Previous Solution" where we should add the dependent variables "H, alphB, alphN". We will also solve initially in a fully coupled manner, meaning that displacements, concentration and phase field variables will be solved simultaneously.

Finally, one should decide what has to be plotted. We create 2D Plot Groups for the phase field, the concentration, the displacements, the stresses and the history field. Surface sub-nodes have to be created in all cases and the variable selected.

Computations run smoothly and one can see the expected trends: (1) the concentration accumulates close to the crack tip, where σ_h is large, (2) the strain energy density is large close to the crack tip and, accordingly so is ϕ, (3) the crack grows towards the centre with the progress of cycling. A representative results for the fatigue crack is shown below:
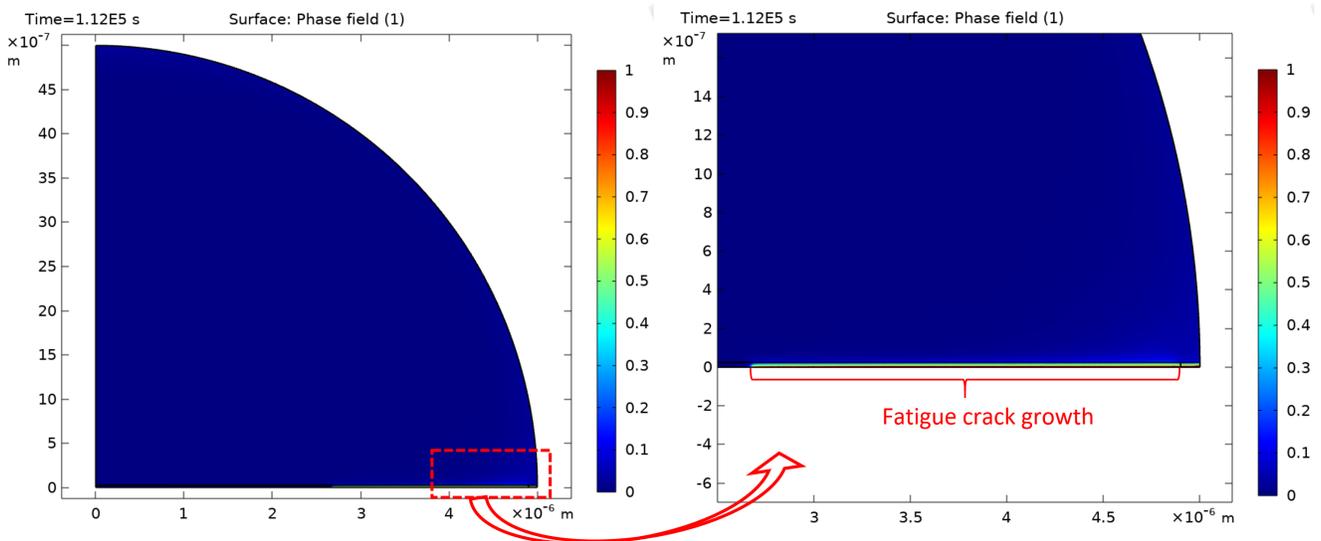

Figure 9: Representative result for a fatigue crack growth.

3. List of files

Note that two files are provided with our code:

- `PhaseFieldFatigueSphere_v5.6.mph`. A representative COMSOL model that enables obtaining the results presented in our paper (see Ref. [12]).

- `PhaseFieldFatigueSphere_v5.6simple.mph`. A model resembling the above but using a coarser mesh, to rapidly obtain results.

Both are developed in version 5.6 and thus can be used with such version or newer ones. Implementations for older versions (5.4 or 5.5) can also be provided upon request.

References

[1] P. K. Kristensen, C. F. Niordson, E. Martínez-Pañeda, An assessment of phase field fracture: crack initiation and growth, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 379 (2021) 20210021.

[2] E. Martínez-Pañeda, A. Golahmar, C. F. Niordson, A phase field formulation for hydrogen assisted cracking, Computer Methods in Applied Mechanics and Engineering 342 (2018) 742–761.

[3] P. K. Kristensen, C. F. Niordson, E. Martínez-Pañeda, A phase field model for elastic-gradient-plastic solids undergoing hydrogen embrittlement, Journal of the Mechanics and Physics of Solids 143 (2020) 104093.

[4] P. K. Kristensen, C. F. Niordson, E. Martínez-Pañeda, Applications of phase field fracture in modelling hydrogen assisted failures, Theoretical and Applied Fracture Mechanics 110 (2020) 102837.

[5] M. Isfandbod, E. Martínez-Pañeda, A mechanism-based multi-trap phase field model for hydrogen assisted fracture, International Journal of Plasticity 144 (2021) 103044.

[6] C. Cui, R. Ma, E. Martínez-Pañeda, A phase field formulation for dissolution-driven stress corrosion cracking, Journal of the Mechanics and Physics of Solids 147 (2021) 104254.

[7] C. Cui, R. Ma, E. Martínez-Pañeda, A generalised, multi-phase-field theory for dissolution-driven stress corrosion cracking and hydrogen embrittlement, Journal of the Mechanics and Physics of Solids 166 (2022) 104951.

[8] M. Klinsmann, D. Rosato, M. Kamlah, R. M. McMeeking, Modeling crack growth during Li extraction in storage particles using a fracture phase field approach, Journal of the Electrochemical Society 163 (2) (2016) A102–A118.

[9] A. M. Boyce, E. Martínez-Pañeda, A. Wade, Y. S. Zhang, J. J. Bailey, T. M. Heenan, P. R. Brett, Dan J. L., Shearing, Cracking predictions of lithium-ion battery electrodes by X-ray computed tomography and modelling, Journal of Power Sources 526 (2022) 231119.

[10] Y. Zhao, R. Wang, E. Martínez-Pañeda, A phase field electro-chemo-mechanical formulation for predicting void evolution at the Li-electrolyte interface in all-solid-state batteries, Journal of the Mechanics and Physics of Solids 167 (2022) 104999.

[11] H. Amor, J. J. Marigo, C. Maurini, Regularized formulation of the variational brittle fracture with unilateral contact: Numerical experiments, Journal of the Mechanics and Physics of Solids 57 (8) (2009) 1209–1229.

[12] W. Ai, B. Wu, E. Martínez-Pañeda, A multi-physics phase field formulation for modelling fatigue cracking in lithium-ion battery electrode particles, Journal of Power Sources 544 (2022) 231805.