PECOS

Predictive Engineering and Computational Sciences

Inadequecy Representation in Models of Supercapacitor Batteries

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Outline

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Governing Equations

electrode

Current density following Ohm's law:

- Matrix phase : $\mathbf{i}_1 = -\sigma\nabla\phi_1$
- Solution phase: $\mathbf{i}_2 = -\kappa\nabla\phi_2$

ϕ_1, ϕ_2: potentials,
σ, κ: electronic/ionic conductivity.

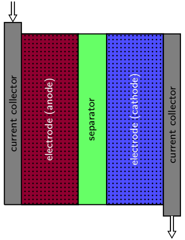
Conservation of charge:

$$-\nabla\cdot\mathbf{i}_1 = \nabla\cdot\mathbf{i}_2 = a i_n$$

a: interfacial area per unit volume
i_n: current transferred from the matrix to the electrolyte

$$i_n = \underbrace{C\frac{\partial}{\partial t}\eta}_{\text{double}-\text{layer}} + \underbrace{i_0\left(\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp\left(-\frac{\alpha_c F}{RT}\eta\right)\right)}_{\text{faradaic}}$$

overpotential: $\eta = \phi_1 - \phi_2$



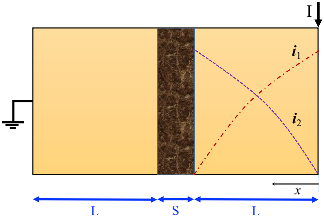
collector

$$\mathbf{i}_1 = -\sigma\nabla\phi_1$$
$$-\nabla\cdot\mathbf{i}_1 = 0$$

seperator

$$\mathbf{i}_2 = -\kappa\nabla\phi_2$$
$$-\nabla\cdot\mathbf{i}_2 = 0$$

High Fidelity Model



- $\eta(\xi, \tau)$ = overpotential in electrode
- $\gamma = \dfrac{\kappa}{\sigma}$: conductivity ratio
- ξ, τ : dimensionless distance/time
- $I(\tau)$: dimensionless current

Modeling Assumptions (Sins)

i. No Faradaic processes: current transferred from matrix to the solution phase goes towards only charging the double-layer at the electrode/electrolyte interface.

ii. ϕ_1 is uniformly distributed over the current collector domain (collector is sufficiently thin)

iii. There is no electron/ion fluxes cross the top and bottom boundaries

iv. The material properties are constant within each layer

High Fidelity model

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial \xi^2}$$

$$\begin{cases} \dfrac{\partial \eta}{\partial \xi}\Big|_{\xi=0} = -\dfrac{\gamma}{1+\gamma} I(\tau) \\ \dfrac{\partial \eta}{\partial \xi}\Big|_{\xi=1} = \dfrac{1}{1+\gamma} I(\tau) \\ \eta\big|_{\tau=0} = \eta_0(\xi) \end{cases}$$

Low Fidelity Model

Modeling Assumptions (Sin)

i. Assuming a quadratically varying profile for overpotential inside the electrodes

$$\eta_{LF}(\xi,\tau) = a(\tau)\xi^2 + b(\tau)\xi + c(\tau)$$

where a, b, and c can be obtained from PDE+BCs of HF model.

Low Fidelity model

$$\eta_{LF}(\xi,\tau) = \frac{1}{2}I(\tau)\xi^2 - I(\tau)\frac{\gamma}{1+\gamma}\xi + \eta^{avg}(\tau) - \frac{I(\tau)}{6} + \frac{I(\tau)}{2}\frac{\gamma}{1+\gamma}$$

η^{avg} is the solution of following ODE given appropriate initial condition:

$$\frac{\partial \eta^{avg}}{\partial \tau} = I(\tau)$$

where η^{avg} is the spatial average of the governing equation over the entire domain length $\eta^{avg} = \int_0^1 \eta d\xi$

QoI : cell voltage

Quantity of Interest

Potential drop across the system

$$\begin{aligned} V^{\text{cell}}(\tau) &= \phi^{L}_{\text{collector}} - \phi^{R}_{\text{collector}} \\ &= 2V_0 - 2V^{\text{elect.}} - V^{\text{sep.}} \end{aligned}$$

where

$$V^{\text{elect.}}(\tau) = \phi_1|_{\xi=0} - \phi_2|_{\xi=1} = \frac{1+2\gamma}{1+\gamma}\eta|_{\xi=1} - \frac{\gamma}{1+\gamma}\eta|_{\xi=0} - \frac{\gamma}{(1+\gamma)^2}I$$

and

$$V^{\text{sep.}}(\tau) = I\frac{L_s}{\kappa_s}$$

Outline

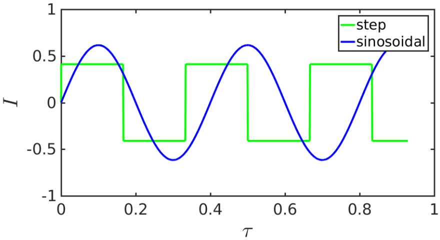
Inadequacy Representation: Objective

Objective:

Based on what we know about the models, develop a representation of inadequacy (*error in QoI*, ϵ) as a parametric model $\mathcal{P}(\boldsymbol{\theta})$ such that

$$V_{\mathrm{HF}}^{\mathrm{cell}} \equiv V_{\mathrm{LF}}^{\mathrm{cell}} + \epsilon$$

- Parameters of inadequacy model, $\boldsymbol{\theta}$, needs to be calibrated using the data furnished by HF model for simple scenarios, e.g.



- $\mathcal{P}(\boldsymbol{\theta})$ enables predicting V^{cell} for more complex scenarios outside the HF data domain along with the associated uncertainty.

Inadequacy Representation

Inadequacy model $\mathcal{P}(\boldsymbol{\theta})$ involves:

- *Deterministic counterpart:* Encapsulates our information about the models.
- *Stochastic counterpart:* Represents the remaining uncertainty due to lack of information about features of full HF system.

Inadequacy Representation

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- *Deterministic counterpart:* Encapsulates our information about the models.
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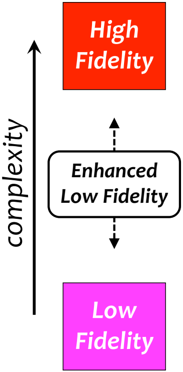


- The goal is to identify a set $\mathcal{M}$ of enhanced low fidelity (ELF) models, with increasing complexity, based on our knowledge about the system,

$$\mathcal{M} = \{\mathcal{P}_1(\boldsymbol{\theta}_1), \mathcal{P}_2(\boldsymbol{\theta}_2), \cdots, \mathcal{P}_n(\boldsymbol{\theta}_n)\},$$

  each model class have its own parameter space $(\boldsymbol{\theta}_k \in \Theta_k)$. Thus,
  - Deterministic $\mathcal{P}^{\mathrm{d}}(\boldsymbol{\theta}^{\mathrm{d}})$: $\epsilon^{\mathrm{d}} = V^{\mathrm{cell}}_{\mathrm{ELF}} - V^{\mathrm{cell}}_{\mathrm{LF}}$
  - Stochastic $\mathcal{P}^{\mathrm{s}}(\boldsymbol{\theta}^{\mathrm{s}})$: $\epsilon^{\mathrm{s}} = V^{\mathrm{cell}}_{\mathrm{HLF}} - V^{\mathrm{cell}}_{\mathrm{ELF}}$
- The more complex ELF model:
  - more complex deterministic $\mathcal{P}^{\mathrm{d}}$ i.e. more parameters
  - more HF data might be required to calibrate
  - less uncertainty in prediction.

Summary of Models and QoI

HF model

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial \xi^2}$$

$$\begin{cases} \frac{\partial \eta}{\partial \xi}|_{\xi=0} = & -\frac{\gamma I}{1+\gamma} \\ \frac{\partial \eta}{\partial \xi}|_{\xi=1} = & \frac{I}{1+\gamma} \\ \eta|_{\tau=0} = & \eta_0(\xi) \end{cases}$$

LF model

$$\eta = \frac{1}{2} I \xi^2 - \frac{I\gamma}{1+\gamma}\xi + \eta^{avg}(\tau) - \frac{I}{6} + \frac{I\gamma}{2(1+\gamma)}$$

QoI: $V_{\mathrm{LF}}(\tau) = \eta^{avg}(\tau) + C_{\mathrm{LF}} I(\tau)$ where

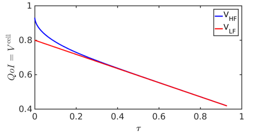
$$\frac{\partial \eta^{avg}}{\partial \tau} = I(\tau)$$

What do we know about HF and LF models?

- Governing equations of HF and LF and the assumptions made to build LF model.
- Model responses in simple cases, e.g. simplified BCs, constant current.
- Any other mathematical/physical information that does not require full solution of HF.

Knowledge about the models

1. HF model is a PDE with *infinite dimensional* solution space (i.e. function space) while LF model is an ODEs having a *finite dimensional* state vector.
2. **Constant current case:** asymptotic behavior of HF is equivalent to LF, i.e. solution of LF converges to HF after a certain time.



3. HF model response dependent on the entire current history, $I(\tau)$, up to time τ. Such history does not appear with right dependency in LF model. *One way to prove this property is through thermodynamics consistency of HF model and Principles of Fading Memory*[a,b].

[a] Coleman, B.D. and E. H. Dill., 1971. Thermodynamic restrictions on the constitutive equations of electromagnetic theory.

[b] Coleman, B.D. and Noll, W., 1961. Foundations of linear viscoelasticity.

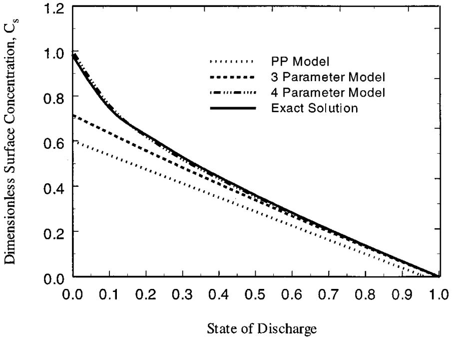
Outline

1 Summary Model Description

2 Inadequecy Representation
- Constructing ELF model
- Deterministic part of inadequacy
- Stochastic part of inadequacy

Constructing ELF model: higher order polynomial

One way to construct ELF is using higher order polynomial functions to approximate the spatial distribution of overpotential.
Subramanian et al.[1] compared the exact solution of a similar PDE+BCs with 2nd, 4th, and 6th order polynomial approximations.



[1] Subramanian, V. R., Ritter, J. A., and White, R. E. (2001). Approximate solutions for galvanostatic discharge of spherical particles i. constant diffusion coefficient. Journal of The Electrochemical Society, 148(11), E444-E449.

Constructing ELF model: DDE

Delay Differential Equations (DDEs):

- DDEs are a large and important class of dynamical systems. They often employed in control problems in which a delay (naturally or technologically) arises between the observation and the control action.
- A simple form of DDEs is an ODE with deviation, $\mathbf{x}'(t) = \mathbf{f}(t, \mathbf{x}(t), \mathbf{x}(t-\tau)),\ \tau > 0$, where τ is a constant time delay.
- ODEs require specifying *initial conditions*, i.e. a small set of numbers indicating the initial values of the state variables at t_0.
  To solve a DDE at every time step, we need to specify an *initial function* $\phi(t), t_0 - \tau \leq t \leq t_0$ which gives the behavior of the system prior to t_0.
- DDEs are *infinite dimensional*:
  To initialize a DDE one must specify the value of state variable over an entire interval (an infinite number of points), thus the manifold of solutions for arbitrary $\phi(t)$ is infinite-dimensional.

Constructing ELF model

LF model

$$V_{\mathrm{LF}}(\tau) = \eta^{avg}(\tau) + C_{\mathrm{LF}} I(\tau)\ ; \qquad \frac{\partial \eta^{avg}}{\partial \tau} = I(\tau),\ \eta^{avg}(0) = 0,\ \tau > 0$$

Constructing ELF model

LF model

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In real system (HF model) the cell potential supposedly reacts not in an instantaneous way to the change in current.

Constructing ELF model

LF model

$$V_{\mathrm{LF}}(\tau) = \eta^{avg}(\tau) + C_{\mathrm{LF}} I(\tau) \; ; \qquad \frac{\partial \eta^{avg}}{\partial \tau} = I(\tau), \; \eta^{avg}(0) = 0, \; \tau > 0$$

In real system (HF model) the cell potential supposedly reacts not in an instantaneous way to the change in current.
We enhance the LF model by creating a delay equation (DDE) and introducing a constant time delay t_s:

ELF model

$$V_{\mathrm{ELF}}(\tau) = \hat{\eta}(\tau) + C_{\mathrm{ELF}} I(\tau - t_s) \; ; \qquad \frac{\partial \hat{\eta}}{\partial \tau} = I(\tau - t_s), \; \hat{\eta}(0) = 0, \; \tau > 0$$

$$\text{Initial Finction} : I(\tau) = \phi(\tau), \; -t_s \le \tau \le 0$$

1. The ELF model (DDEs) belong to the class of systems with the functional state, similar to PDEs are infinite dimensional.
2. ELF model, to some extend, bring the history information of the current.
3. The asymptotic behavior of ELF model is equivalent to LF and HF models.

Outline

Inadequacy Representation: Deterministic

- Deterministic $\mathcal{P}^{\mathrm{d}}(\boldsymbol{\theta})$: $\epsilon^{\mathrm{d}} = V^{\mathrm{cell}}_{\mathrm{ELF}} - V^{\mathrm{cell}}_{\mathrm{LF}}$
- The objective is not to solve the full ELF system, rather using it to motivates a mathematical form for inadequacy model.
- Using Taylor expansion:

$$V_{\mathrm{ELF}}(\tau) = \hat{\eta}(\tau) + C_{\mathrm{ELF}}\left(I(\tau) - t_s \frac{\partial I}{\partial \tau} + \frac{1}{2} t_s^2 \frac{\partial^2 I}{\partial \tau^2} + \cdots \right)$$

with

$$\frac{\partial \hat{\eta}}{\partial \tau} = I(\tau) - t \frac{\partial^2 \hat{\eta}}{\partial \tau^2} - \frac{1}{2} t_s^2 \frac{\partial^3 \hat{\eta}}{\partial \tau^3} + \cdots$$

- One can increase the complexity of the ELF and corresponding $\mathcal{P}^{\mathrm{d}}$ by considering more Taylor expansion terms.

Inadequacy Representation: Deterministic

Constructing $\mathcal{P}_1^{\mathrm{d}}(\boldsymbol{\theta})$ using one Taylor expansion term of ELF:

$$V_{\mathrm{LF}} = \eta^{avg} + C_{\mathrm{LF}} I \quad \text{with} \quad \frac{\partial \eta^{avg}}{\partial \tau} = I$$

$$V_{\mathrm{ELF}} = \hat{\eta} + C_{\mathrm{ELF}}(I - t_s \frac{\partial I}{\partial \tau}) \quad \text{with} \quad \frac{\partial \hat{\eta}}{\partial \tau} = I - t_s \frac{\partial^2 \hat{\eta}}{\partial \tau^2}$$

Substituting above relations in $\epsilon_1^{\mathrm{d}} = V_{\mathrm{ELF}} - V_{\mathrm{LF}}$ and evaluating $\dfrac{\partial \epsilon_1^{\mathrm{d}}}{\partial \tau}$ and little manipulation, one can derive:

$$\mathcal{P}_1^{\mathrm{d}}(\boldsymbol{\theta}_1^{\mathrm{d}}) : \quad \frac{\partial \epsilon_1^{\mathrm{d}}}{\partial \tau} + \lambda^2 \epsilon_1^{\mathrm{d}} = \alpha \frac{\partial I}{\partial \tau} + \beta I$$

where $\boldsymbol{\theta}_1^{\mathrm{d}} = (\lambda, \alpha, \beta)$ needs to be calibrated against HF data.

Inadequacy Representation: Deterministic

Using second terms of the Taylor expansions, and following similar derivation, motivates an inadequacy representation such as:

$$\mathcal{P}_2^{\mathrm{d}}(\boldsymbol{\theta}_2^{\mathrm{d}}): \quad \frac{\partial^2 \epsilon_2^{\mathrm{d}}}{\partial \tau^2} + \lambda^2 \frac{\partial \epsilon_2^{\mathrm{d}}}{\partial \tau} + \mu^2 \epsilon_2^{\mathrm{d}} = \alpha I + \beta \frac{\partial I}{\partial \tau} + \rho \frac{\partial^2 I}{\partial \tau^2}$$

writing the above relation as system of 1st order ODEs

$$\mathcal{P}_2^{\mathrm{d}}(\boldsymbol{\theta}_2^{\mathrm{d}}): \begin{cases} x_1'(\tau) = & x_2(\tau) \\ x_2'(\tau) = & \mathcal{I}(\tau) \quad -\mu^2 x_1(\tau) - \lambda^2 x_2(\tau) \end{cases}$$

where $\epsilon_2^{\mathrm{d}} = x_1(\tau)$

and $\mathcal{I}(\tau) = \alpha I + \beta \dfrac{\partial I}{\partial \tau} + \rho \dfrac{\partial^2 I}{\partial \tau^2}$

where $\boldsymbol{\theta}_2^{\mathrm{d}} = (\lambda, \mu, \alpha, \beta, \rho)$ needs to be calibrated against HF data.

Inadequacy Representation: Deterministic

Constant current case:

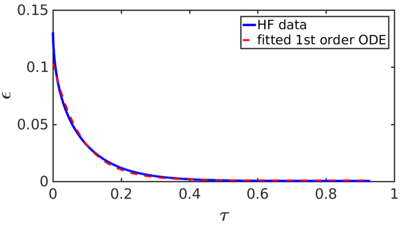
Under constant current assumption, it can be easily shown that

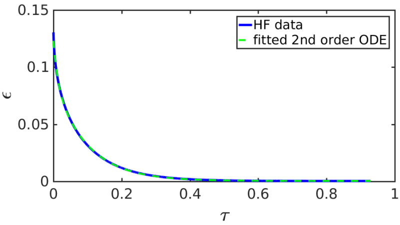
$$V_{\mathrm{ELF}} \equiv V_{\mathrm{LF}} + \sum_{i=1}^{n} C_i \exp(-\frac{\tau}{t_i})$$

where number of terms in the Prony series n determine the complexity of the ELF model.

Also, it is trivial to prove that $V_{\mathrm{ELF}} \to V_{\mathrm{HF}}$ as $n \to \infty$.

Calibrating against HF data:





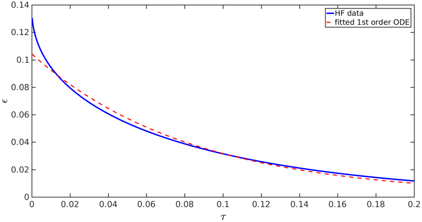
Inadequacy Representation: Deterministic

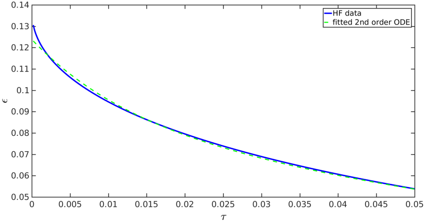
Constant current case:

Calibrating inadequacy models against HF data:

$\mathcal{P}_1^{\mathrm{d}} : \lambda = 3.47, \beta = 0.0223$ $\mathcal{P}_2^{\mathrm{d}} : \lambda = 9.55, \mu = 28.82, \alpha = 0.532$

If finite number of exponential decay enhancements, n, is taken into account for constructing ELF, the motivated inadequacy model is incapable of capturing HF data in a small time scale.



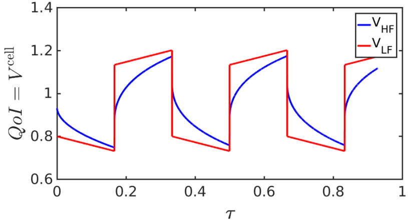


Similar results are also expected for step current case, for a small time scale right after I switches.

It should be noted that, for physical point of view, in very short time even the HF might not be represent the reality, due to the simplifying assumptions made to construct HF model.

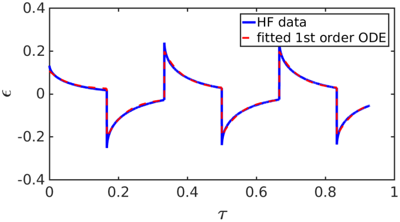
Inadequacy Representation: Deterministic

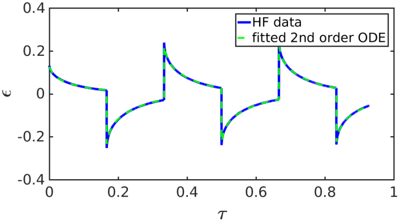
Step current case:



Calibrating inadequacy models against HF data:

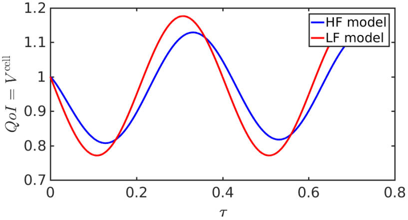
- $\mathcal{P}_1^{\mathrm{d}} : \lambda = 4.2273, \beta = 0.8766, \alpha = 0.2764$
- $\mathcal{P}_2^{\mathrm{d}} : \lambda = 10.64, \mu = 34.03, \alpha = 9.018, \beta = 23.9858, \rho = 0.3048$

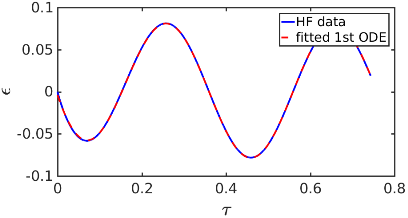


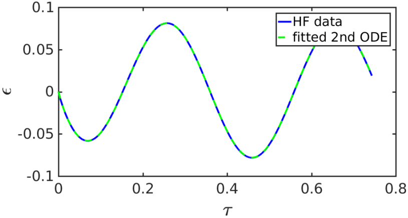


Inadequacy Representation: Deterministic

Sinusoidal current case: Low Frequency

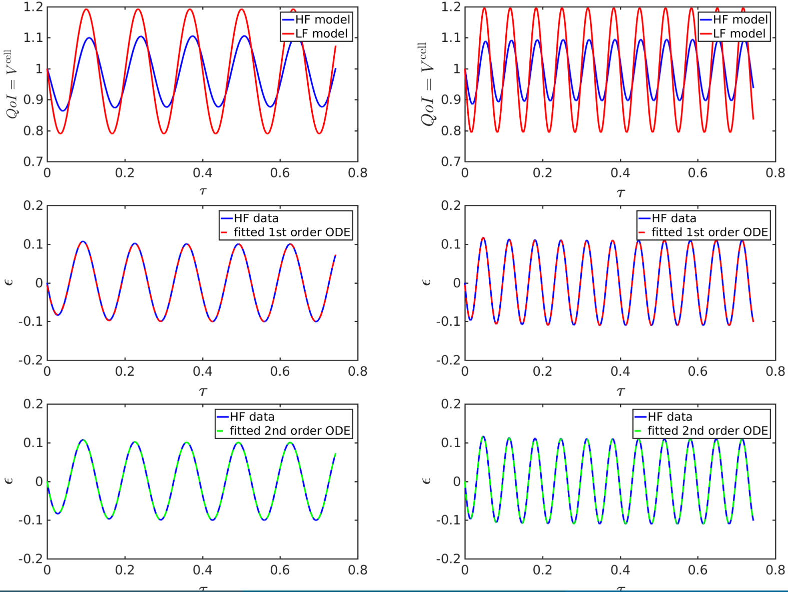






Inadequacy Representation: Deterministic

Sinusoidal current case: Intermediate and High Frequency



Inadequacy Representation: Deterministic

Sinusoidal current case: Different current frequencies

		Low Freq.	Inter Freq.	error*	High Freq.	error*
$\mathcal{P}_1^{\mathrm{d}}$	λ	3.3459	3.8389	-0.147	4.7179	-0.410
	β	0.0932	0.134	-0.440	0.035	0.624
	α	-0.2352	-0.2555	-0.086	-0.2746	-0.167
$\mathcal{P}_2^{\mathrm{d}}$	λ	8.8651	9.4434	-0.0652	7.6434	0.138
	μ	26.6081	29.7492	-0.118	32.298	-0.214
	α	36.35	38.39	-0.0561	40.94	-0.126
	β	-15.38	-18	-0.17	-20.93	-0.361
	ρ	0.1415	0.2079	-0.4693	0.2801	-0.979

*error = relative error wrt parameters of Low Freq

If we calibrate $\mathcal{P}^{\mathrm{d}}$ against HF data obtained from low frequency scenario

- The deterministic inadequacy representation enables predicting the intermediate frequency scenario.
- It break down for predicting the high frequency scenario.

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