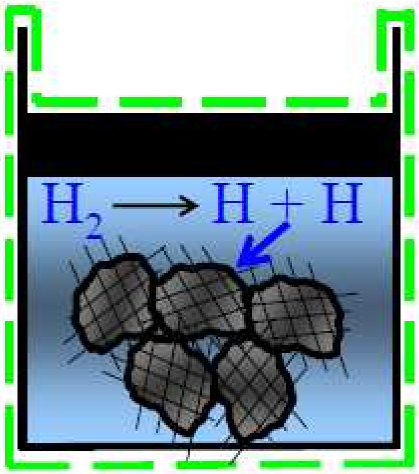
Weierstrass Institute for
Applied Analysis and Stochastics

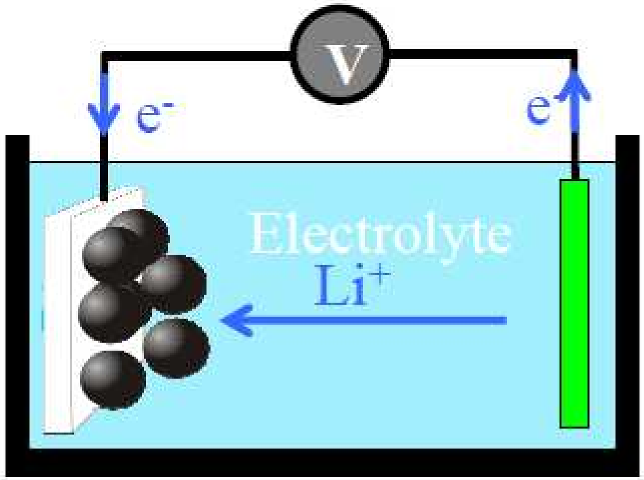
Leibniz Gemeinschaft

Modeling of the Nonlocal and Nonlinear Material Behavior of Many-Particle Electrodes

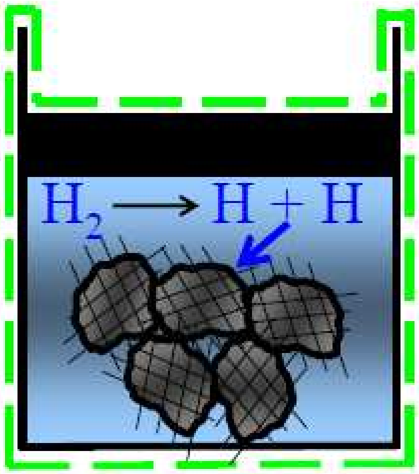
Wolfgang Dreyer & Clemens Guhlke

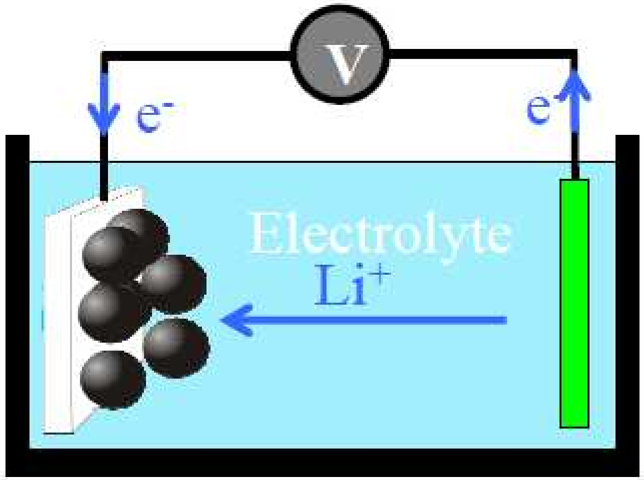


$H_2 \longrightarrow H + H$



V
e-
e-
Electrolyte
Li+


H2 → H + H


V
e-
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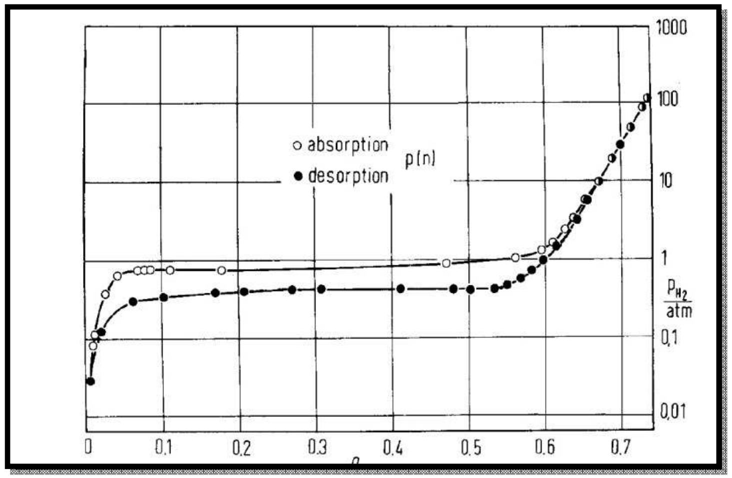
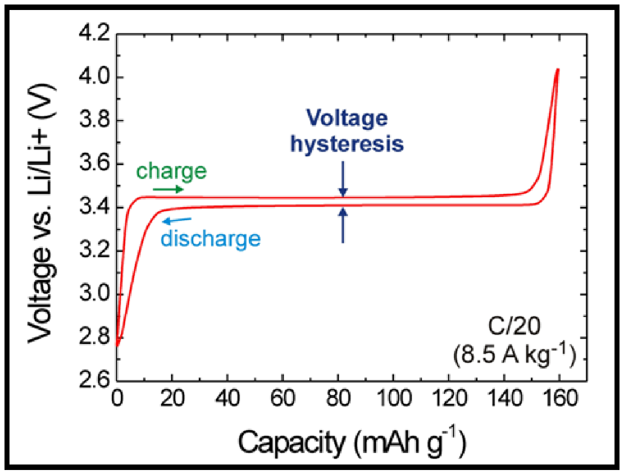
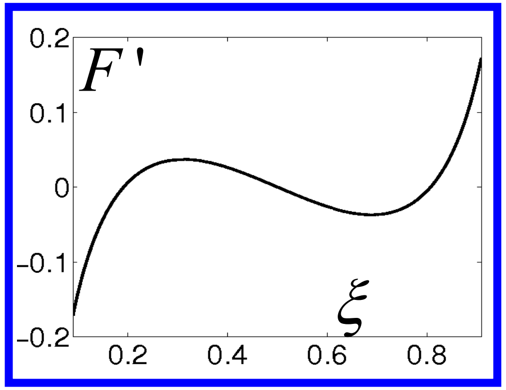

○ absorption
● desorption
p(n)
1000
100
10
1
0,1
0,01
PH2 / atm
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7


Voltage vs. Li/Li+ (V)
Capacity (mAh g-1)
Voltage hysteresis
charge
discharge
C/20
(8.5 A kg-1)
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
0
20
40
60
80
100
120
140
160

$$\xi \in [a,b] \quad t \geq 0$$

$$\tau \frac{\partial w(t,\xi)}{\partial t} + \frac{\partial(\Lambda(t)G'(\xi) - F'(\xi))w(t,\xi)}{\partial \xi} = \nu^2 \frac{\partial^2 w(t,\xi)}{\partial \xi^2}$$

$$q(t) = \int_a^b G(\xi) w(t,\xi)\, d\xi$$

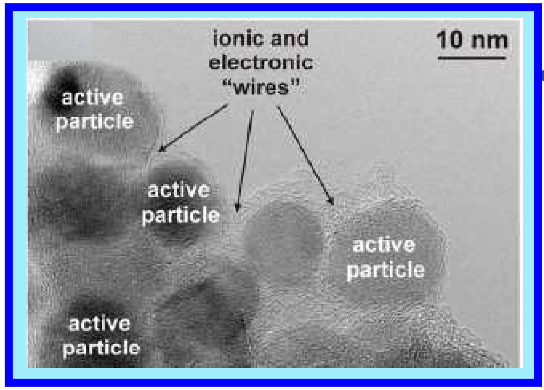


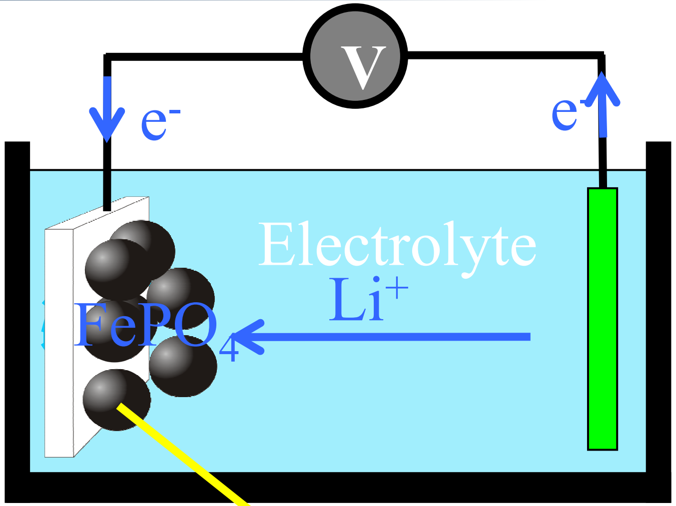
$$w(\xi,0) = w_0(\xi)$$

$$\big(\Lambda(t)G'(a) - F'(a)\big)w(t,a) - \nu^2 \partial_\xi w(t,a) = 0$$

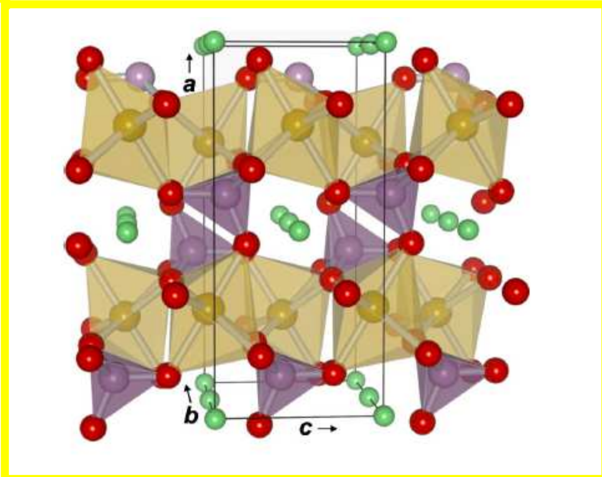
$$\big(\Lambda(t)G'(b) - F'(b)\big)w(t,b) - \nu^2 \partial_\xi w(t,b) = 0$$

Functionality of modern Li-ion batteries

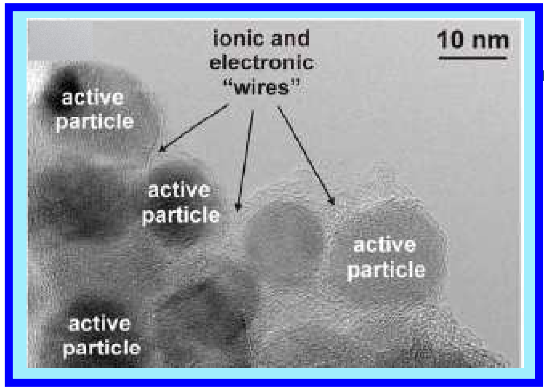


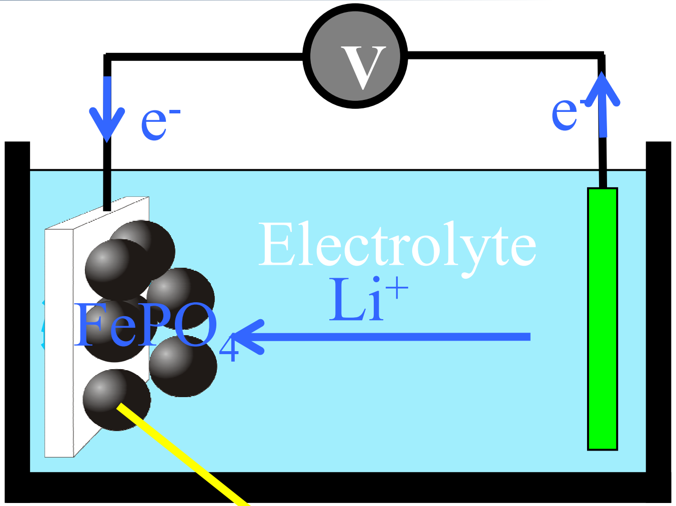


FePO$_4$ with orthorhombic symmetry

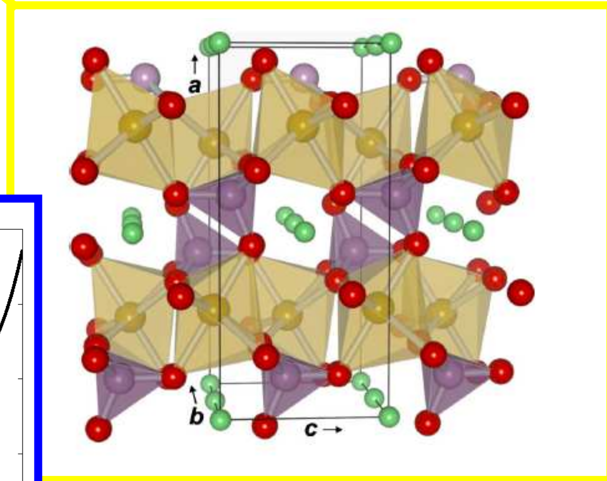


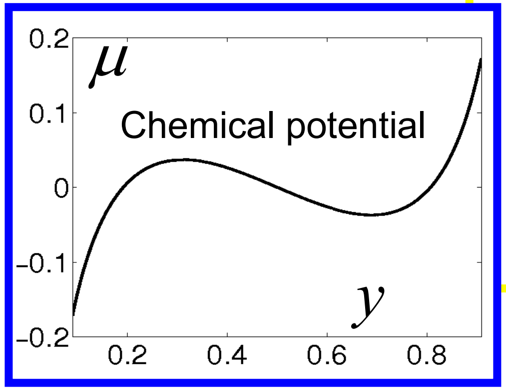
Functionality of modern Li-ion batteries



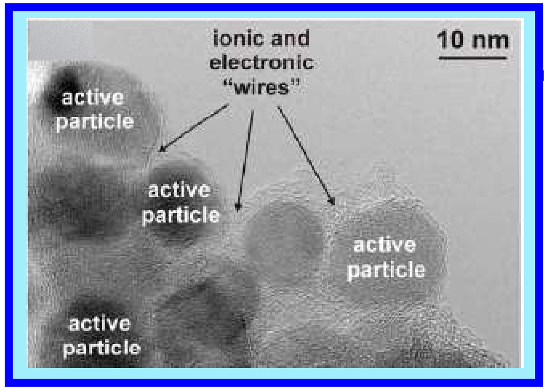


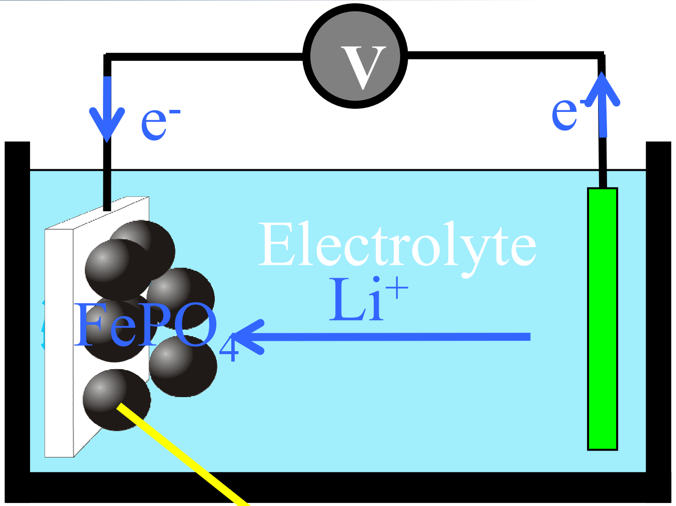
Li_yFePO_4 with orthorhombic symmetry



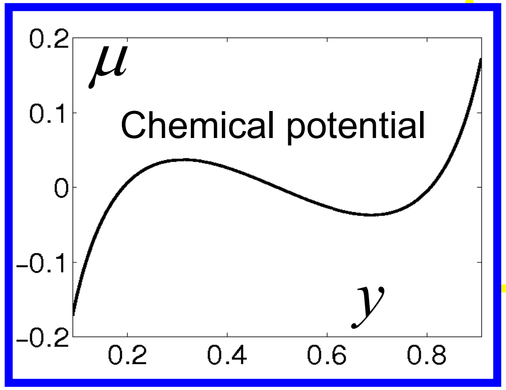


Functionality of modern Li-ion batteries

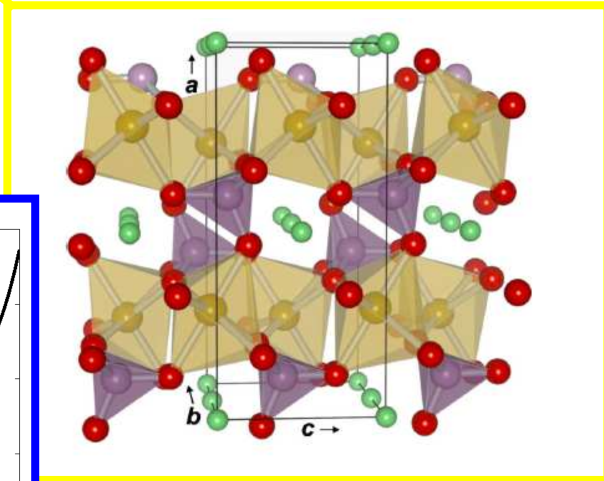


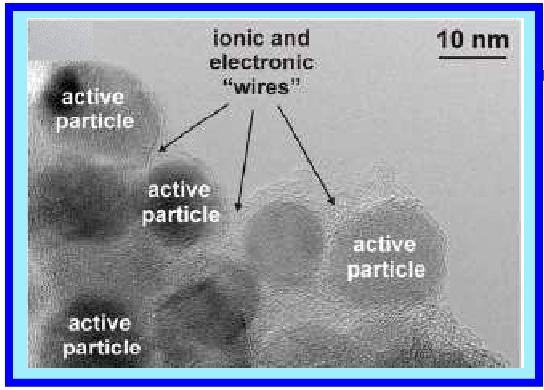


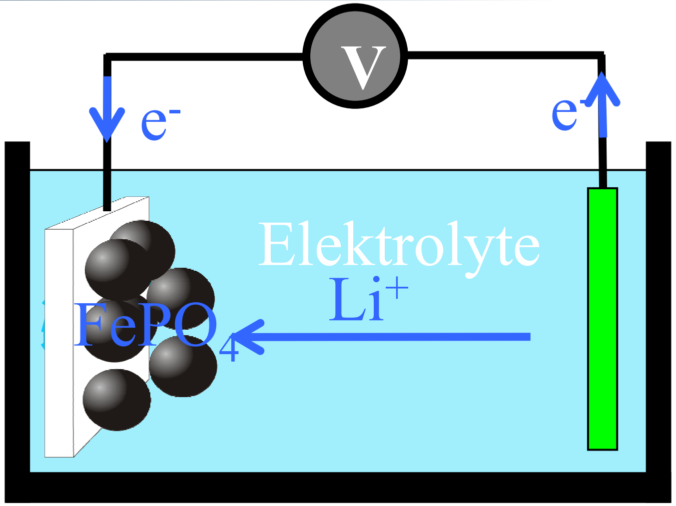
$$V(t) = -\frac{1}{e} < \mu > (t) + V_0$$



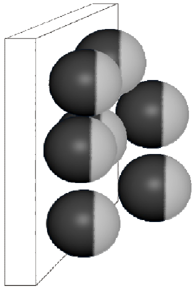
Li_yFePO_4 with orthorhombic symmetry







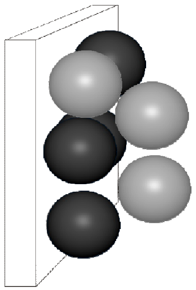
How does the lithium storage process work ?



Scenario 1

Phase transition within particles

Simultaneous charging of particles



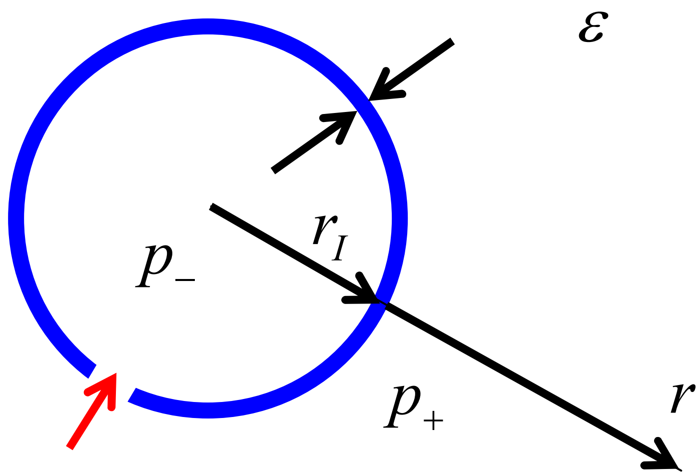
Scenario 2

Homogeneous particles

Phase transition within many-particle system

Charging by the rule: One after the other

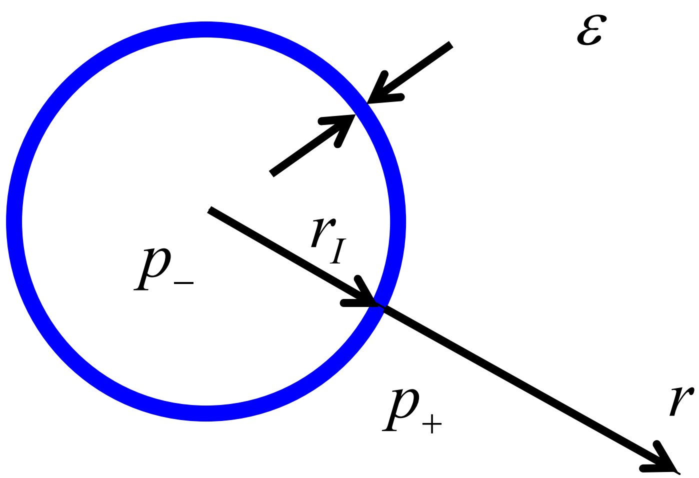
Non-monotonicity in a single elastic rubber balloon



Non-monotonicity in a single elastic rubber balloon

Sharp limit of 3D non-linear elliptic elasticity problem

$$p_- - p_+ = \varepsilon\left(\frac{r_0}{r_I} - \left(\frac{r_0}{r_I}\right)^7\right)\left(1 + \frac{1}{10}\left(\frac{r_I}{r_0}\right)^2\right)$$



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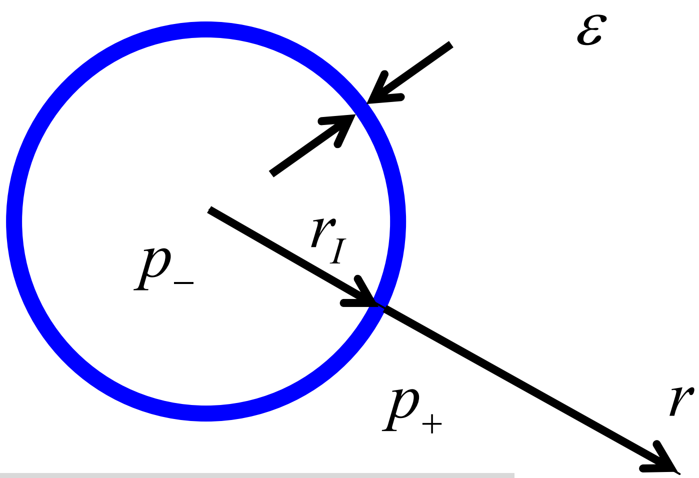
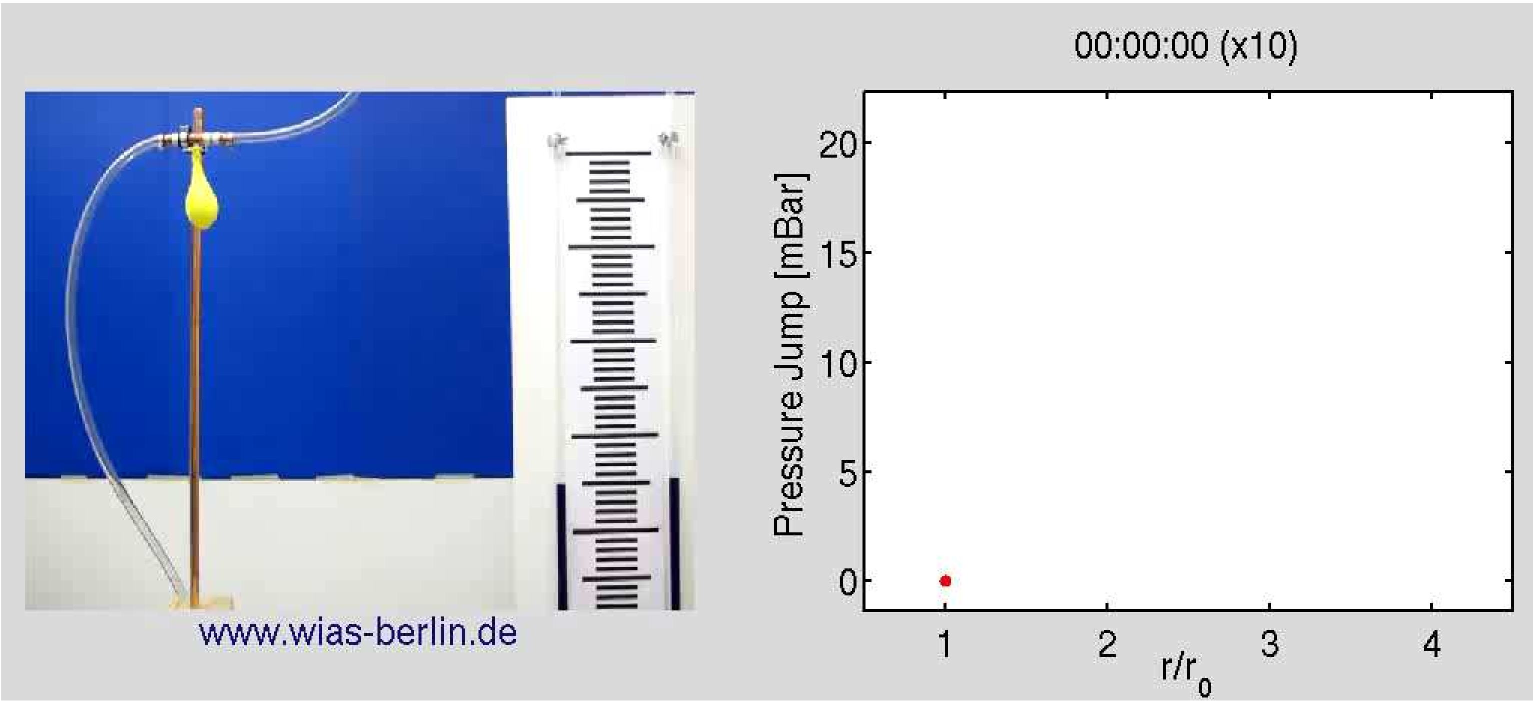
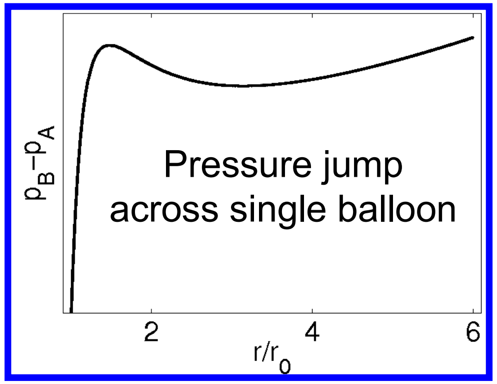




Many-particle effect of the balloon system: *One after the other* !



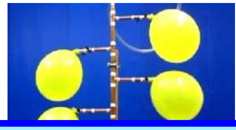
Evolution equation of Fokker-Planck type

- $$\tau \frac{\partial w(t,\xi)}{\partial t} + \frac{\partial(\Lambda(t)G'(\xi) - F'(\xi))w(t,\xi)}{\partial \xi} = \nu^2 \frac{\partial^2 w(t,\xi)}{\partial \xi^2}$$
- $\Lambda(t)$ from $q(t) = \int_a^b G(\xi) w(t,\xi)\, d\xi$

Evolution equation of Fokker-Planck type

$$\tau\frac{\partial w(t,\xi)}{\partial t}+\frac{\partial(\Lambda(t)G'(\xi)-F'(\xi))w(t,\xi)}{\partial\xi}=\nu^2\frac{\partial^2 w(t,\xi)}{\partial\xi^2}$$

$\Lambda(t)$ from $q(t)=\int_a^b G(\xi)w(t,\xi)\,d\xi$

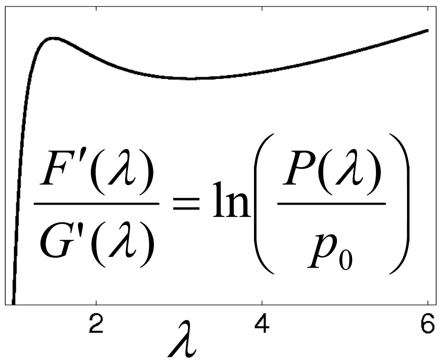


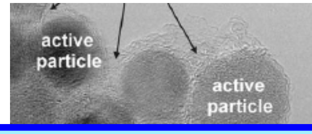
Balloon system

$\xi=\lambda$ Strain of single balloon

q Total amount of air

$G(\lambda)$ Monotone function



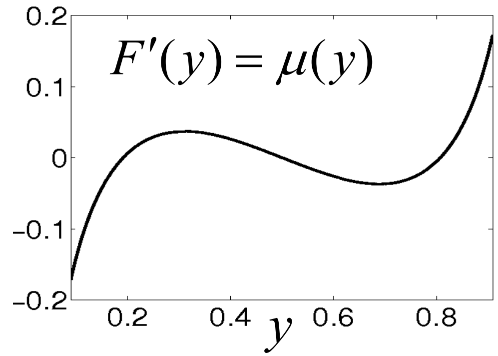


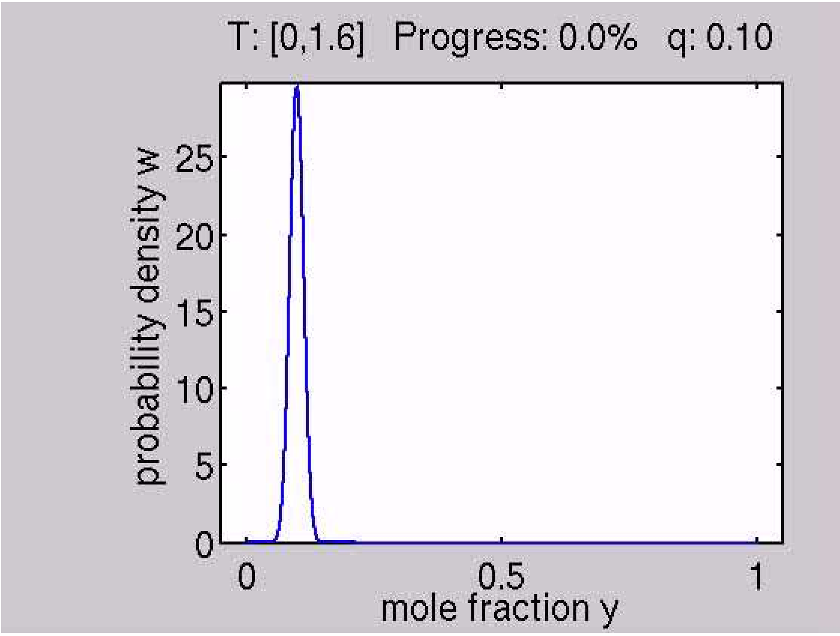
Lithium-ion battery

$\xi=y$ Lithium concentration

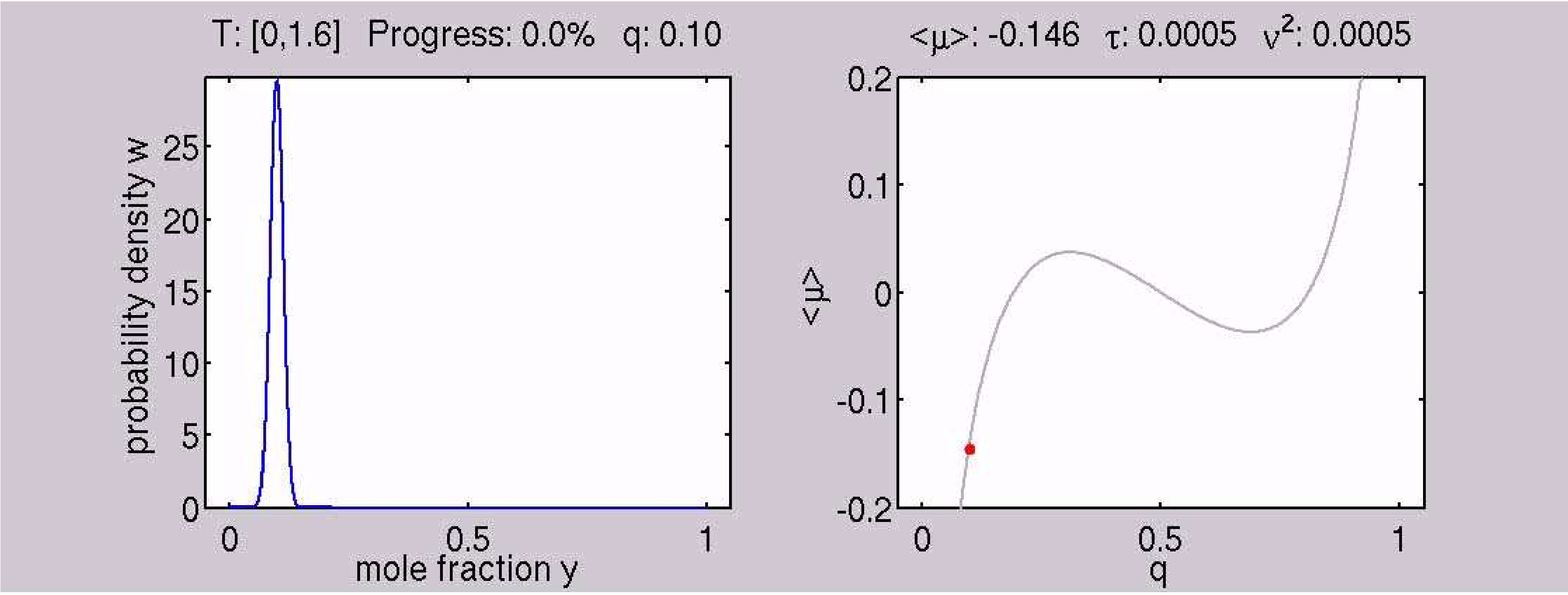
q Total amount of lithium

$G(y)=y$

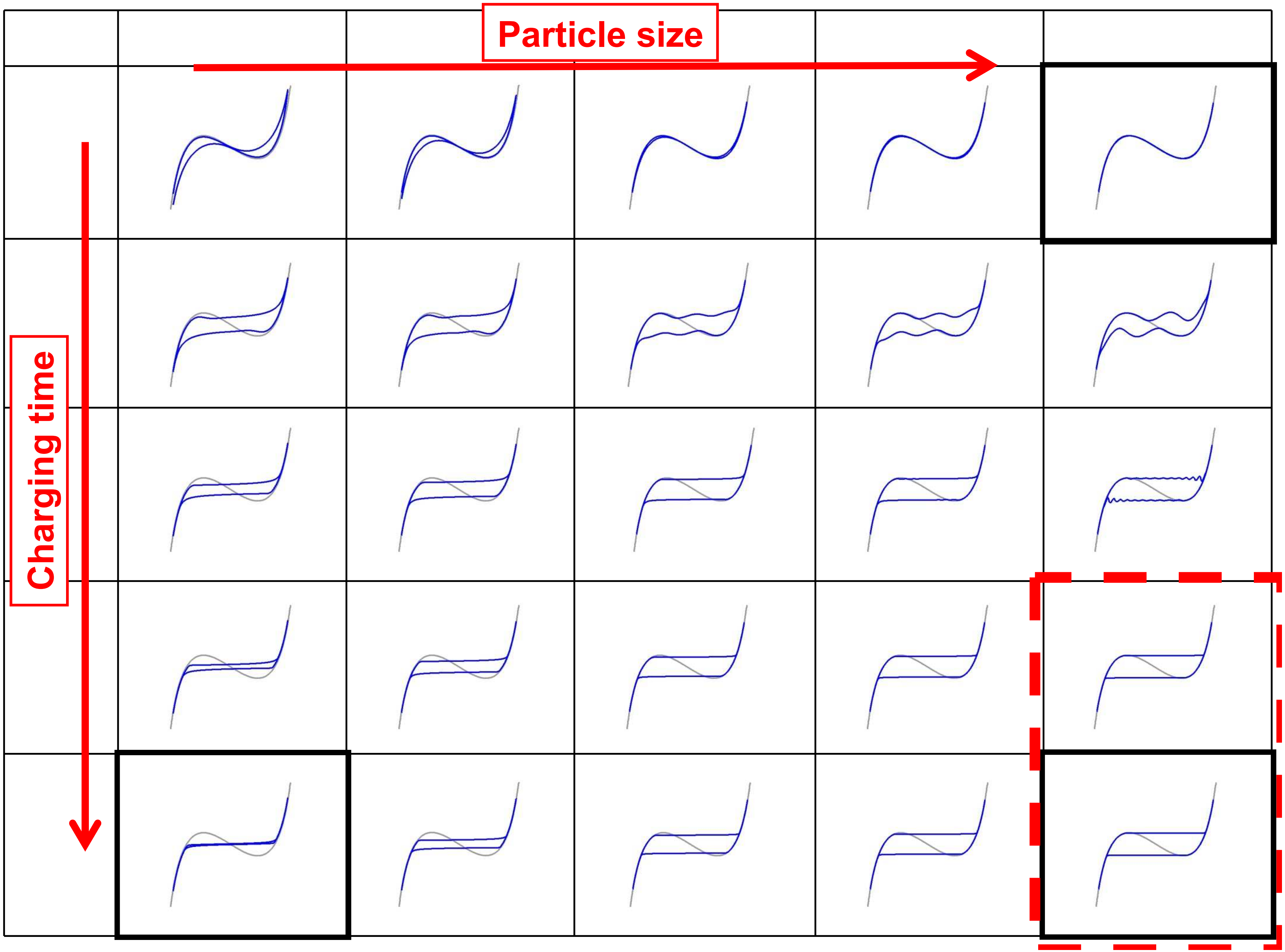


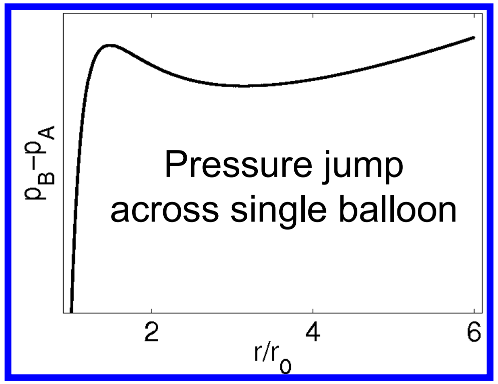


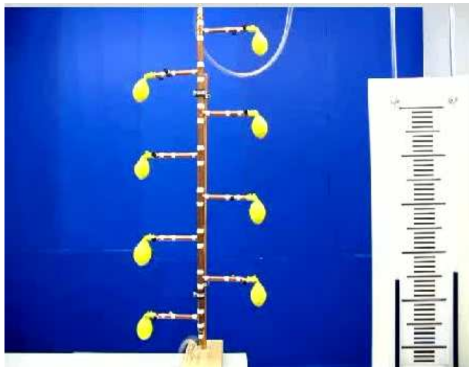
$$q(t) = \int_0^1 y w(t,y)\, dy$$

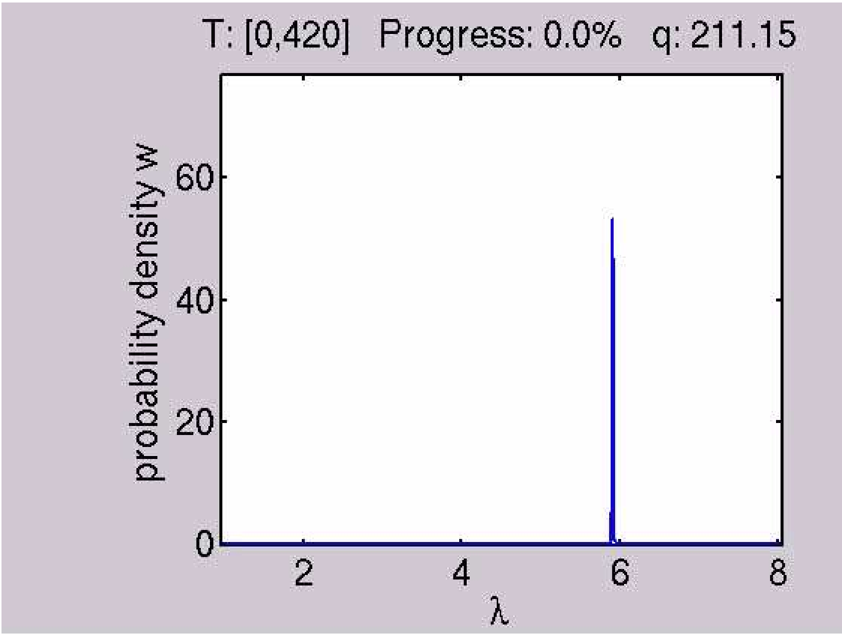


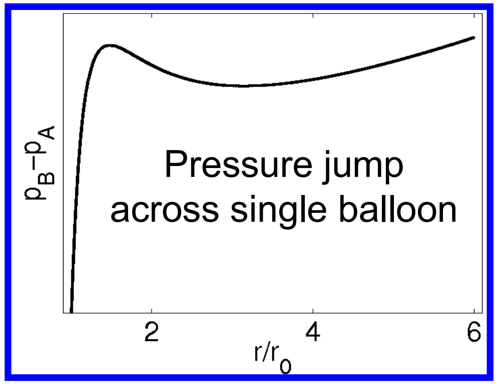
$$q(t) = \int_0^1 y\, w(t,y)\, dy \qquad \langle \mu \rangle (t) = \int_0^1 \mu(y)\, w(t,y)\, dy$$

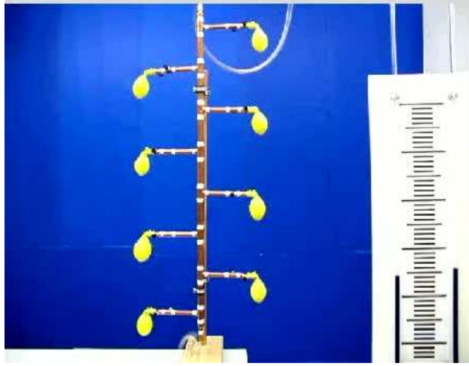

Particle size
Charging time

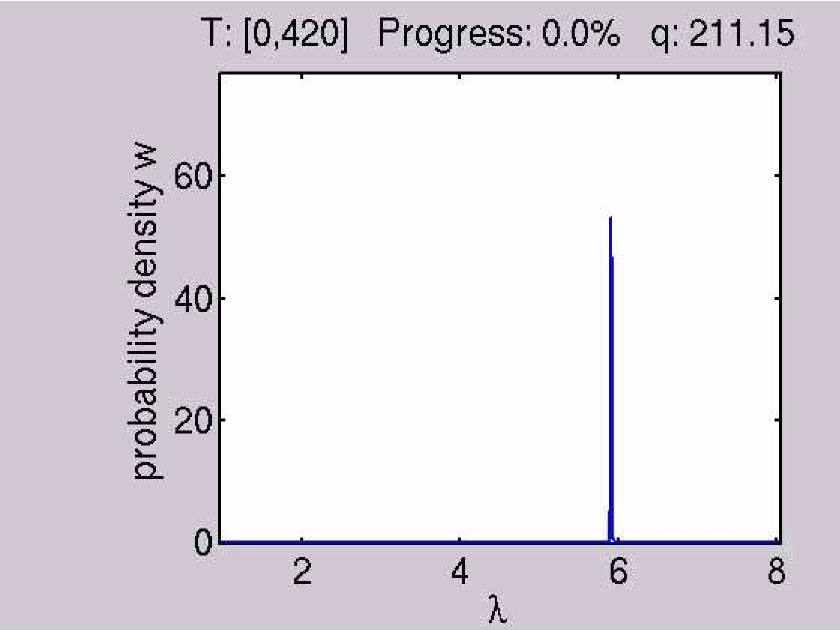

Pressure jump
across single balloon
$p_B - p_A$
r/r_0
2
4
6




T: [0,420] Progress: 0.0% q: 211.15
probability density w
0
20
40
60
2
4
6
8
λ

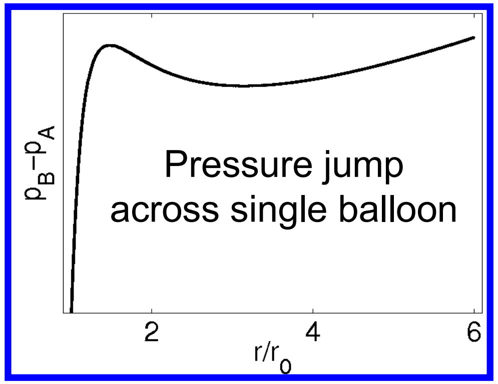


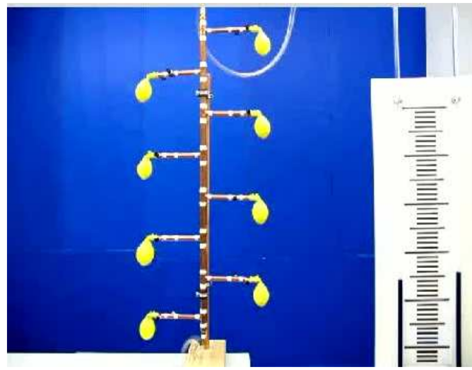


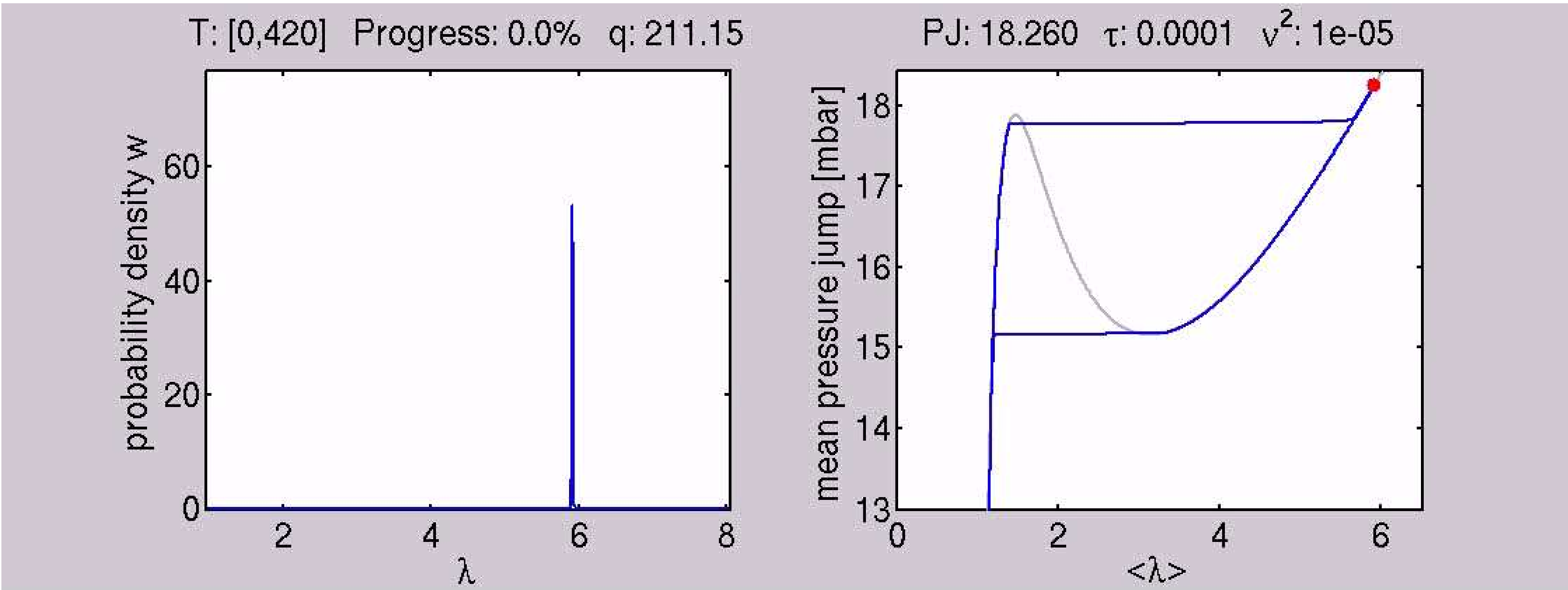


$$\langle \lambda \rangle (t) = \int_1^{\lambda_*} \lambda w(t,\lambda)\, d\lambda$$

$$\langle P \rangle (t) = \int_1^{\lambda_*} P(\lambda) w(t,\lambda)\, d\lambda$$







$$\langle \lambda \rangle (t) = \int_1^{\lambda_*} \lambda w(t,\lambda)\, d\lambda \qquad \langle P \rangle (t) = \int_1^{\lambda_*} P(\lambda) w(t,\lambda)\, d\lambda$$

Thermodynamic inequality for isothermal processes

2nd Law of Thermodynamics for isothermal open systems

$$\frac{d\mathcal{A}}{dt} - \Lambda \frac{dq}{dt} \leq 0$$

Thermodynamic inequality for isothermal processes

2nd Law of Thermodynamics for open systems

$$\frac{d\mathcal{A}}{dt} - \Lambda \frac{dq}{dt} \leq 0$$

$\mathcal{A} =$ Sum over individual free energies of the storage particle

$-T*$ Brownian entropy of the many-particle system

Thermodynamic inequality for isothermal processes

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$-T *$ Brownian entropy of the many-particle system

Total free energy

$$\mathcal{A}(w) = \int_a^b (F(\xi) w(t,\xi) + \nu^2 w(t,\xi) \log w(t,\xi)) d\xi$$

Thermodynamic inequality for isothermal processes

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Side conditions

$$q(t) = \int_a^b G(\xi) w(t,\xi)\, d\xi \qquad 1 = \int_a^b w(t,\xi)\, d\xi \qquad w(t,\xi) \geq 0$$

Thermodynamic inequality for isothermal processes

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$$\longrightarrow \quad \int_a^b \left(F(\xi) - \Lambda(t)G(\xi) + \nu^2(1 + \log w(t,\xi))\right)\frac{\partial w(t,\xi)}{\partial t}d\xi \leq 0$$

Thermodynamic inequality for isothermal processes

2nd Law of Thermodynamics for open systems

$$\frac{d\mathcal{A}}{dt} - \Lambda \frac{dq}{dt} \leq 0$$

Structure of PDE

$$\frac{\partial w(t,\xi)}{\partial t} + \frac{\partial \upsilon(t,\xi)\, w(t,\xi)}{\partial \xi} = 0$$

Total free energy

$$\mathcal{A}\left(w\right) = \int_a^b (F(\xi) w(t,\xi) + \nu^2 w(t,\xi) \log w(t,\xi))\, d\xi$$

Side conditions

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Thermodynamic inequality for isothermal processes

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$$q(t) = \int_a^b G(\xi) w(t,\xi)\, d\xi \qquad 1 = \int_a^b w(t,\xi)\, d\xi \qquad w(t,\xi) \ge 0$$

$$\longrightarrow \int_a^b \left(F'(\xi) - \Lambda(t) G'(\xi) + \nu^2 \frac{\partial \log w(t,\xi)}{\partial \xi} \right) \upsilon(t,\xi)\, w(t,\xi)\, d\xi \le 0$$

Thermodynamic inequality for isothermal processes

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Structure of PDE

$$\frac{\partial w(t,\xi)}{\partial t} + \frac{\partial \upsilon(t,\xi)\, w(t,\xi)}{\partial \xi} = 0$$

Total free energy

$$\mathcal{A}\left(w\right) = \int_a^b (F($$

Simplest possibility to statisfy the inequality

$$\tau \upsilon(t,\xi) = \Lambda(t) G'(\xi) - F'(\xi) - \nu^2 \frac{\partial \log w(t,\xi)}{\partial \xi}$$

Side conditions

$$q(t) = \int_a^b G(\xi) w(t,\xi) d\xi \qquad 1 = \int_a^b w(t,\xi)\, d\xi \qquad w(t,\xi) \geq 0$$

$$\longrightarrow \int_a^b \left(F'(\xi) - \Lambda(t) G'(\xi) + \nu^2 \frac{\partial \log w(t,\xi)}{\partial \xi}\right) \upsilon(t,\xi)\, w(t,\xi)\, d\xi \leq 0$$

$$\nu \to 0 \quad \tau \to 0$$

$$\xi \in [a,b] \quad t \geq 0$$

$$\tau \frac{\partial w(t,\xi)}{\partial t} + \frac{\partial(\Lambda(t)G'(\xi) - F'(\xi))w(t,\xi)}{\partial \xi} = \nu^2 \frac{\partial^2 w(t,\xi)}{\partial \xi^2}$$

$$q(t) = \int_a^b G(\xi) w(t,\xi)\, d\xi$$

$$w(\xi,t) = w_0(\xi)$$

$$\big(\Lambda(t)G'(a) - F'(a)\big)w(t,a) - \nu^2 \partial_\xi w(t,a) = 0$$

$$\big(\Lambda(t)G'(b) - F'(b)\big)w(t,b) - \nu^2 \partial_\xi w(t,b) = 0$$

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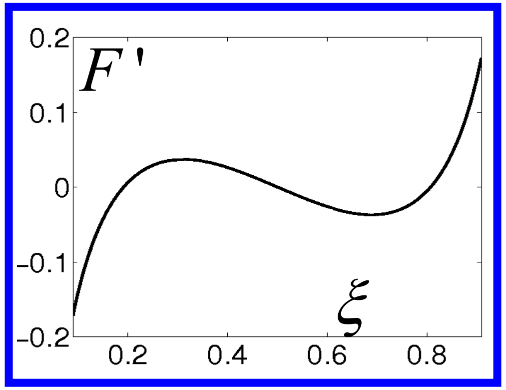


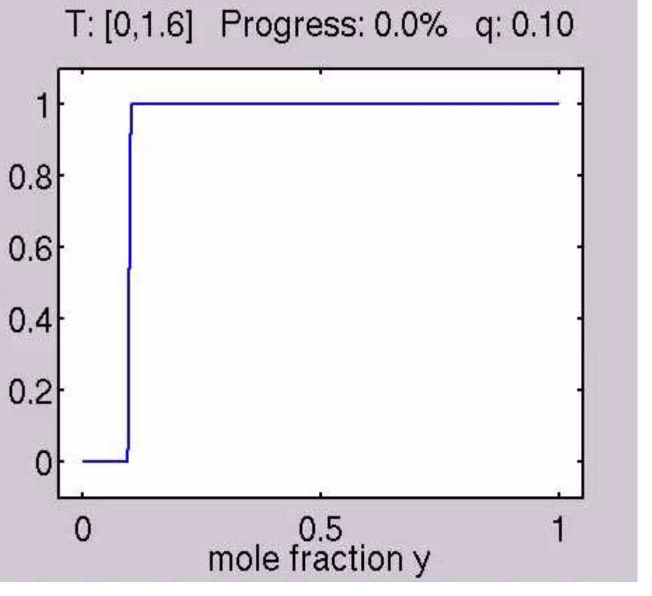
$$w(\xi,t) = w_0(\xi)$$

$$\left(\Lambda(t)G'(a) - F'(a)\right)w(t,a) - \nu^2 \partial_\xi w(t,a) = 0$$

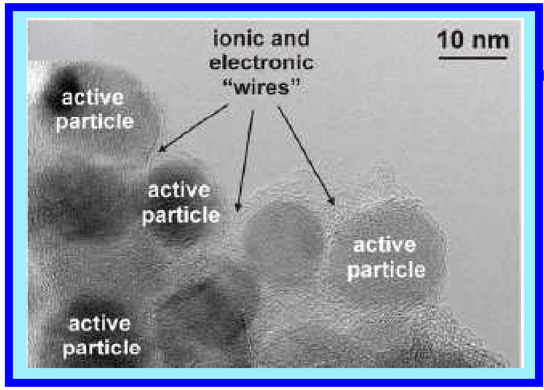
$$\left(\Lambda(t)G'(b) - F'(b)\right)w(t,b) - \nu^2 \partial_\xi w(t,b) = 0$$

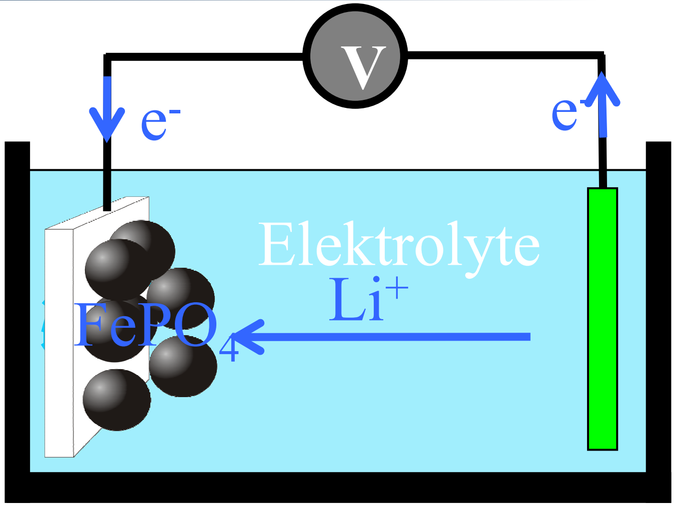
Def. $$g(\xi,t) = \int_0^{\xi} w(y,t)\,dy$$

Lemma If the initial condition $g(\xi,0)$ is monotone increasing, then $g(\xi,t)$ preserves this property for $t \in [0,T]$

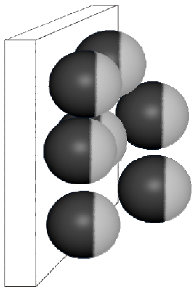


Functionality of modern Li-ion batteries





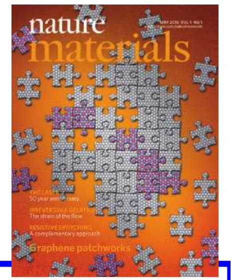
How does the lithium storage process work ?



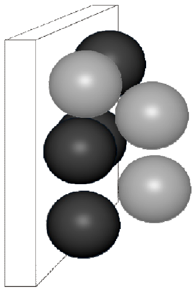
Scenario 1

Phase transition within particles ?

Simultaneous charging of particles ?



The thermodynamic origin of hysteresis in insertion batteries
W. Dreyer, J. Jamnik, C. Guhlke, R. Huth, J. Maškon, M. Gaberšček
Nature Materials Volume 9 No 5 (2010), pp448 – 453



Scenario 2

Homogeneous particles ?

Phase transition within many-particle system ?

Charging by the rule: One after the other ?