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The behavior of a many particle cathode in a lithium-ion battery

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Abstract

We study the almost reversible storage process of charging and discharging of lithium-ion batteries. That process is accompanied by a phase transition and charging and discharging run along different paths, so that hysteretic behavior is observed.

We are interested in the storage problem of the cathode of a lithium-ion battery consisting of a system of many iron phosphate ($FePO_4$) particles. There are mathematical models, see [2], [3] and [4], that describe phase transitions and hysteresis exclusively in a single storage particle and they can describe the observed hysteretic voltage-charge plots with almost horizontal plateaus. Interestingly the models predict that the coexistence of a 2-phase system in an individual particle disappears, if its size is below a critical value. The disappearance of the phase transition in the single particle model implies the disappearance of the hysteresis. However, in the experiment hysteretic behavior survives. In other words: The behavior of a storage system consisting of many particles is qualitatively independent of the fact whether the individual particles itself develop a 2-phase system or if they remain in a single phase state.

This apparent paradoxical observation will be resolved in this article by a many particle model. It will be shown that if each of the individual particles is in a homogeneous state, nevertheless the many particle ensemble exhibits phase transition and hysteresis, because one of the two phases is realized in some part of the particles while the remaining particles are in the other phase. Mathematically speaking this phenomenon is due to the non-monotonicity of the relation between the chemical potential and the lithium mole fraction.

The pressure-radius relation of a spherical elastic rubber balloon also exhibits non-monotone behavior. In fact, a system of many interconnected balloons behaves correspondingly to a cathode consisting of many storage particles. This analogy between the two systems is important, because the predictions of the many particle model can easier be tested with rubber balloons of macroscopic size than with an ensemble of microscopically small ($FePO_4$) particles.

1 Introduction and basic functionality of rechargeable lithium-ion batteries

Currently rechargeable lithium-ion batteries are the most promising storage systems for electrical energy.

The charging and discharging process is accompanied by a phase transition and it exhibits hysteretic behavior, which is described in a characteristic diagram, see Figure 1, that gives the voltage of the battery cell versus its total charge.

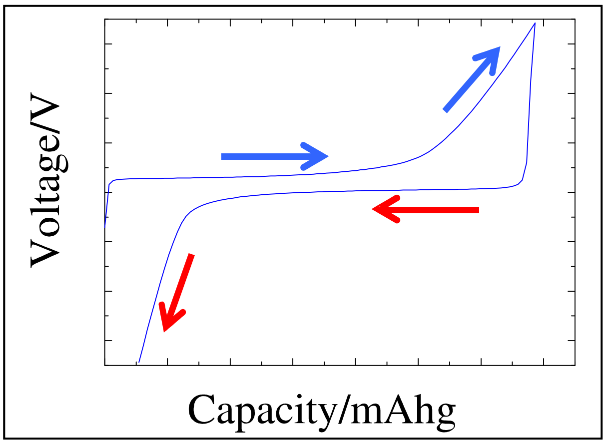

Figure 1: Voltage versus charge per mass of a $FePO_4$ cathode [2]

The cathode of lithium-ion batteries is designed as a storage system for lithium atoms, which consists of many small iron phosphate ($FePO_4$) crystalline particles forming a layer on a substrate. The interstitial lattice sites of $FePO_4$ serve to store the lithium atoms. In the fully charged state of the battery, there is no lithium in the storage system while it contains the maximal possible number of lithium atoms when the battery is fully discharged.

We consider two versions of a simplified battery cell as they are sketched in Figure 2. The device on the left hand side of Figure 2 contains a many-particle storage system, whereas on its right hand side the cathode consists of a single storage particle. Both versions consider the storage particles as small spheres of about 50 nm diameter, thus these are not of macroscopic size. Figure 2 also indicates the processes in a

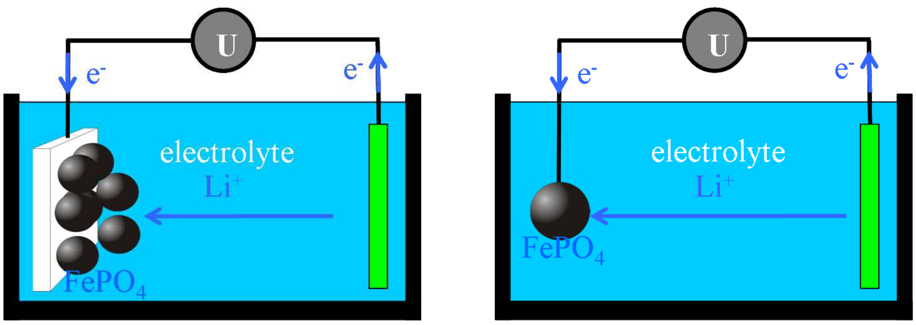

Figure 2: $FePO_4$ particles against an metallic Li anode within an electrolyte.

lithium battery during discharging and charging. During discharging electrons leave the anode to travel through an outer circuit. The remaining positive lithium ions leave the anode and move through the electrolyte towards the cathode, where they recombine with the incoming electron at the carbon coated surface of the storage particles.

In a single storage particle we have the following situation. For small lithium content, the lithium atoms form a single phase that we call α-phase. However, if the lithium content of the storage particle exceeds a certain value and if the particle is not too small, the formation of a second phase, β-phase, sets in. The single particle model predicts that the voltage remains constant in the coexistence region of the two phases, see Figure 1.

A further phenomenon that occurs is a reversible and elastic change of the particle volume during charging and discharging, which is due to the fact that the lithium atoms need more space as is available by the interstitial lattice sites in $FePO_4$. During lithium storage the volume typically changes up to 6%.

The mathematical model, that were proposed in [2], [3] and [4], describe phase transitions and hysteresis exclusively in a single particle. On that basis they are able to show that the observed horizontal plateaus can be a consequence of the coexistence of two phases which differ by high and small lithium concentrations in a single particle. Further theoretical studies on the evolution of lithium atoms in a single particle system by Han et al. [7], Srinivasan and Newman [15] also rely on this phenomenon, which is experimentally investigated by Yamada et al. [18].

Surprisingly there is the following observation. When the size of an individual particle becomes too small the coexistence region vanishes and the particle remains in a single phase state. This fact is observed in experiments, see Wagemaker et al. [17], and it also results from the model equations in [2], [3] and [4].

However, in the experiment hysteretic behavior survives. The key idea to explain this strange behavior relies on the fact that in the experiment we always meet a many particle cathode.

Delmas et al. [5] report on detailed experimental observations concerning the statement of Wagemaker et al. [17]. They study an ensemble of storage particles with sizes within the range from 80 nm to 150 nm. Here they exclusively found particles either in α- or in β- phase. This fact lead them to the conjecture that only few particles are in the state of two coexistent phases. They develop an interesting model, that describes the mechanism of the phase transition in a many storage particle system. In the current study we propose a mathematical model that is capable to predict the observations by Delmas et.al. in a very natural way.

We will show that the non-monotonicity of the chemical potential function with respect to the lithium concentration of a single storage particle implies the hysteretic behavior of a many particle system, where its members are single phase storage particles.

A similar non-monotonicity occurs in the paper on rate independent hysteresis by Truskinovski and Puglisi in a different context. They aim to explain hysteretic phenomena in shape memory alloys on a microscopic basis, [14]. Their microscopic model is a one-dimensional chain of N oscillators, where each oscillator is equipped with a non-monotone stress-strain relation. Further differences to the study of this paper are boundary conditions during the cycling of the hysteresis loop and the mathematical treatment.

The same subject is currently under investigation by Mielke and Truskinovski, [11]. In order to reduce the necessary assumptions which are needed in a quasi-static treatment of the problem. The authors rely their new reasoning of the behavior of the chain model according to an evolution law, and in addition to the non-monotone stress-strain relation they provide the oscillators with viscous elements and stochastic behavior.

The analysis of a many particle system, where each particle is equipped with unstable states between two stable states, has already been started in 1982 by Dreyer, Müller and Strehlow, [6], where the equilibria of two interconnected spherical and elastic rubber balloons were studied. That problem was generalized to $N > 2$ interconnected balloons by Kitsche, [8] in his diploma thesis, and the results, which form a complete analogy to the current problem and to Truskinovski and Puglisi, were published in [9] in 1987, see also Chapter 5 for a detailed discussion of the analogy between the behavior of the many particle cathode of a lithium-ion battery and a large number of interconnected rubber balloons.

The paper is organized as follows: In Chapter 2 we introduce the basic properties of the storage particles. Chapter 3 introduces the thermodynamic model. Chapter 4 is addressed to the detailed exploitation of a simplified model for lithium storage. Here we numerically illustrate the various phenomena and carry out the mathematical analysis. Finally we have added a small Chapter 5, where we explain the intimate analogy between the many particle storage problems and the problem of the inflation of many connected rubber balloons.

2 Crystal structure and basic variables of the host systems

In this chapter we describe the crystal structure of the $FePO_4$ and identify the basic variables that are needed to describe the thermodynamic state of the storage system. However, for the purposes of the current study we will end up with a simplified description, and we refer the reader to the given citations for the complete and more precise details.

2.1 Crystal structure of $FePO_4$ for lithium storage

The crystal lattice of an $FePO_4$ particle is illustrated in Figure 3. The $FePO_4$ units are indicated by yellow (Fe), pink (P), red (O) and the green balls are the interstitial lattice sites that can be occupied by the lithium atoms. The deformation of the

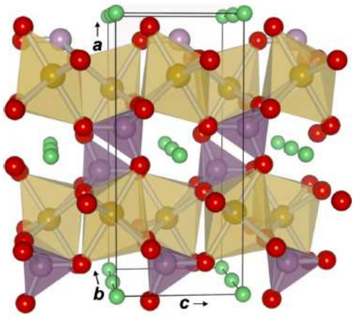

Figure 3: $FePO_4$ structure. Yellow: Fe, pink: P, red: O, green: interstitial sites. From [10]

lattice during the loading of the storage system with lithium atoms is described in detail by T. Maxisch and G. Ceder in [10]. The undeformed crystal has orthorhombic olivine symmetry. In this state the sublattice, formed by the interstitial lattice sites, is completely empty. To each unit of $FePO_4$ there corresponds one single site in the sublattice. The olivine structure does not change during the occupation of the sublattice sites by lithium atoms. When these are supplied or removed through the external boundary, there is a deformation of the olivine structure, because the lithium atoms need more space as is available by the sublattice sites. Thus the crystal volume changes if the number of lithium atoms is changed. Moreover the stiffness coefficients change.

2.2 Basic variables for lithium storage

The number N_{M} of $FePO_4$ units, which form the matrix lattice, is fixed. Thus we assume that there is no diffusion in the matrix lattice but it is deformed, and for simplicity we only take the change of its volume V into account and ignore deviatoric stresses, see [2] concerning the complete mechanical description.

On the sublattice of a particle we have N_{Li} lithium atoms and N_{V} vacancies. The latter indicate the empty lattice sites, which do not have mass or momentum but they are carrier of energy and entropy. Since there is a single sublattice site to each $FePO_4$ unit, we have the side condition

$$N_{\mathrm{M}} = N_{\mathrm{Li}} + N_{\mathrm{V}}. \tag{1}$$

Thus for given temperature T, the basic variables of the lithium storage problem are V, N_{M} and N_{Li}. For the local description we introduce the mole densities n_{M}, n_{Li} and n_{V} which have units mole/m^3. Note that n_{M} changes because the volume V may change, whereas N_{M} is constant.

3 A piece of thermodynamics of the storage particles

In this chapter we introduce those basic facts of thermodynamics that are needed.

3.1 Thermodynamics of a single storage particle

Global inequality. We consider a single $FePO_4$ particle, see Figure 2. For constant temperature and fixed external pressure or fixed volume the 1st and 2nd law of thermodynamics imply for a system, that does not exchange lithium atoms with the surrounding, the temporal inequality

$$\frac{dA}{dt} \leq 0 \quad \text{with} \quad A = \Psi + p_0 V. \tag{2}$$

The quantity A is the available free energy of the storage particle, which occupies a spatial domain $\Omega(t)$, and it is given by the (Helmholtz) free energy Ψ plus outer pressure p_0 times the total volume V of the particle, provided that the kinetic energy is ignored.

In equilibrium the equality sign holds, whereas the available free energy must exclusively decrease in non-equilibrium. Possible equilibria are thus determined by the minima of A.

The application of the inequality (2) to the cases at hand requires some discussion in advance. Whatever the initial state of the storage particle is, the inequality describes the evolution of that state to equilibrium, provided, that the given side conditions are satisfied. In this study we are interested in processes that are induced by loading and unloading of the storage particle with lithium atoms. Thus the considered system does exchange matter with the surrounding. In this case the form (2) of the thermodynamic inequality is only applicable for *quasi-static* loading and unloading. This means that the interior processes run on a much faster time scale than the evolution of $N_{\mathrm{Li}}(t)$.

Free energy density, chemical potentials, pressure, Gibbs equation and Gibbs-Duhem equation. The total free energy Ψ of a storage particle is an additive quantity that can be written as

$$\Psi = \int_{\Omega} \rho \psi \, dx. \tag{3}$$

Here ρ is the mass density and ψ denotes the specific free energy of the particle.

We have $\rho = m_{\mathrm{M}} n_{\mathrm{M}} + m_{\mathrm{Li}} n_{\mathrm{Li}} = n_{\mathrm{M}}(m_{\mathrm{M}} + m_{\mathrm{Li}} y)$, where m_{M} and m_{Li} are the molecular masses of $FePO_4$ and Li, respectively, and $y = n_{\mathrm{Li}}/n_{\mathrm{M}}$ gives the lithium mole fraction.

The specific free energy is given by a constitutive function that relates ψ to the temperature T, which is a constant in this study, and to the mole densities n_{Li}, n_{V}

of lithium and vacancies. Since we have $n_{\mathrm{M}} = n_{\mathrm{Li}} + n_{\mathrm{V}}$, the latter dependence can also be described by the lithium mole fraction y and the mole density of the matrix units n_{M}:

$$\psi = \psi(T, n_{\mathrm{Li}}, n_{\mathrm{V}}) = \tilde{\psi}(T, y, n_M). \tag{4}$$

The representation via the function $\tilde{\psi}$ simply results from a transformation of the variables.

The free energy density satisfies the Gibbs equation and the Gibbs-Duhem equations, see [1] and [12]. These read

$$d\rho\psi = -\rho s dT + \sum_{a\in(\mathrm{Li},\mathrm{V})} \mu_a dn_a \quad \text{and} \quad p = -\rho\psi + \sum_{a\in(\mathrm{Li},\mathrm{V})} \mu_a n_a, \tag{5}$$

where the newly introduced quantities are the chemical potentials μ_a and the pressure p. From (5) and by an easy calculation we obtain the constitutive relations

$$\mu_a = \frac{\partial\rho\psi}{\partial n_a}\ , \quad \mu_{\mathrm{Li}} - \mu_{\mathrm{V}} = m_{\mathrm{Li}}\tilde{\psi} + (m_{\mathrm{M}} + m_{\mathrm{Li}}y)\frac{\partial\tilde{\psi}}{\partial y}\ , \quad p = -\rho\tilde{\psi} + n_{\mathrm{M}}\frac{\partial\rho\tilde{\psi}}{\partial n_{\mathrm{M}}}\ . \tag{6}$$

The representations (6) are of central importance in the following.

3.2 The available free energy of a many particle system

Now we consider the many particle problem as indicated in Figure 2_{left}. The considered system contains N storage particles, indexed by $l \in 1, 2, ..., N$. A storage particle l has the volume V^l, N^l_{M} $FePO_4$ units forming the matrix lattice and N^l_{Li} lithium atoms on the interstitial lattice. The further characterization of the many particle ensemble relies on three conditions.

(i) We assume that each particle is in a homogeneous state.

(ii) The number N^l_{M} of matrix molecules ($FePO_4$) is constant and the same for each storage particle $N^l_{\mathrm{M}} = N^1_{\mathrm{M}}, l = 1, \ldots, N$.

(iii) The unloaded particles all have the same volume $V^l = \bar{V}, l = 1, \ldots, N$ and thus the same mole density $\bar{n}_{\mathrm{M}}$.

The available free energy for the N particle system is given by

$$A = \sum_{l=1}^{N} \int_{\Omega_l} \rho^l \psi^l \ dx + V p_0 = \sum_{l=1}^{N} V^l(\rho^l\psi^l + p_0) \tag{7}$$

where $V = \sum_{l=1}^{N} V^l$ is the total volume of the system.

Furthermore we introduce the total numbers of matrix units and of lithium content of the ensemble.

$$N^l_{\mathrm{M}} = n^l_{\mathrm{M}} V^l = \bar{n}_{\mathrm{M}} \bar{V}, \qquad N^l_{\mathrm{Li}} = n^l_{\mathrm{Li}} V^l, \tag{8}$$

$$N_{\mathrm{M}} = \sum_{l=1}^{N} N^l_{\mathrm{M}} = N \bar{n}_{\mathrm{M}} \bar{V}, \qquad N_{\mathrm{Li}} = \sum_{l=1}^{N} N^l_{\mathrm{Li}} \tag{9}$$

The macroscopic filling degree $q = N_{\mathrm{Li}}/N_{\mathrm{M}}$ denotes the overall loading state of the system, which can be written as

$$q = \frac{\sum_{l=1}^{N} N^l_{\mathrm{Li}}}{N_{\mathrm{M}}} = \frac{1}{N} \sum_{l=1}^{N} y^l \ . \tag{10}$$

Necessary conditions for equilibria. According to (4), (7) and $(8)_1$ the available free energy A depends on the variables $(y^l, n^l_{\mathrm{M}})_{l\in\{1,2,\ldots,N\}}$. Recall that we study the quasi-static case. We thus seek for equilibria at given filling degree q. We get rid of the condition (10) by the introduction of a Lagrange multiplier λ. There are two kinds of necessary conditions for equilibrium:

$$\frac{\partial A^*}{\partial n^l_{\mathrm{M}}} = 0 \ , \quad \frac{\partial A^*}{\partial y^l} = 0 \quad \text{with} \quad A^* = A - \lambda\Big(\sum_{i=1}^{N} y^i - Nq\Big) \ . \tag{11}$$

The conditions $(11)_1$ and $(11)_2$ determine mechanical equilibrium respectively chemical equilibrium, and by means of (7) and (6) we obtain for mechanical equilibrium

$$p(y^l, n^l_{\mathrm{M}}) = p_0 \qquad \text{for all} \quad l = 1, \ldots, N \ , \tag{12}$$

where p_0 is the external pressure on the particle surfaces, and for chemical equilibrium

$$\mu_{\mathrm{Li}}(y^l, n^l_{\mathrm{M}}) - \mu_{\mathrm{V}}(y^l, n^l_{\mathrm{M}}) = \mu_{\mathrm{Li}}(y^N, n^N_{\mathrm{M}}) - \mu_{\mathrm{V}}(y^N, n^N_{\mathrm{M}}) \tag{13}$$

for all $l = 1, \ldots, (N-1)$. Later, we will see that this condition implies that the voltage of all particles is the same.

The explicit evaluation of the necessary conditions for equilibrium requires constitutive equations for the specific free energies.

3.3 Simplified version of explicit constitutive equations

Section 3.1 reveals that the explicit knowledge of the specific free energy allows to calculate the chemical potentials and the pressure as well. The strategy to determine the specific free energy, i.e. $\psi = \psi(T, n_{\mathrm{Li}}, n_{\mathrm{V}}) = \tilde{\psi}(T, y, n_{\mathrm{M}})$, relies on the observation that we may additively decompose $\rho\psi$ into a chemical and a mechanical part:

$$\rho\psi = \rho\tilde{\psi}^{\mathrm{chem}}(T, y, n_{\mathrm{M}}) + \rho\tilde{\psi}^{\mathrm{mech}}(T, y, n_{\mathrm{M}}) \quad \text{with} \quad \tilde{\psi}^{\mathrm{mech}}(T, y=0, \bar{n}_{\mathrm{M}}) = 0. \tag{14}$$

The motivation of that decomposition relies on the fact, that our knowledge on the two contributions to the free energy originates from different sources.

Constitutive functions for the pressure. The storage particles are assumed to be elastic with misfit strain, which is due to the variation of their volume during loading and unloading. The misfit strain is given by $h(y) = 1/(1+\delta y)$ with $\delta = (V_{\max} - \bar{V})/\bar{V}$, and a simple constitutive law for the pressure p of a particle is assumed to be given by

$$p = \bar{p} + K(y)\left(\frac{n_{\mathrm{M}}}{\bar{n}_{\mathrm{M}}} - h(y)\right). \tag{15}$$

We have $\delta \approx 0.067$ for lithium storage. $\bar{p}$ is the reference pressure, $V_{\max}$ denotes the volume of a storage particle with maximal loading and $\bar{V}$ denotes the reference volume, which is assumed by an unloaded particle. Finally $K(y)$ denotes the concentration dependent bulk modulus. However, that dependence will be ignored here and so K is a constant.

Mechanical part of the free energy. By integration of $(6)_3$ we obtain the mechanical part of the free energy density of the particles

$$\rho\tilde{\psi}^{\mathrm{mech}} = (p_{\mathrm{R}} - Kh(y))\left(\frac{n_{\mathrm{M}}}{\bar{n}_{\mathrm{M}}h(y)} - 1\right) + K\frac{n_{\mathrm{M}}}{\bar{n}_{\mathrm{M}}}\log\left(\frac{n_{\mathrm{M}}}{\bar{n}_{\mathrm{M}}h(y)}\right), \tag{16}$$

where the integration constant is chosen so that $\rho\psi^{\mathrm{mech}}(y = 0, n_{\mathrm{M}} = \bar{n}_{\mathrm{M}}) = 0$.

Chemical part of free energies. We use here the same non-convex constitutive law as in [2], which takes entropy of mixing and the heat of solution into account. It reads

$$\rho\tilde{\psi}^{\mathrm{chem}} = n_{\mathrm{M}} L f(y) \tag{17}$$

with

$$f(y) = y(1-y) + \frac{RT}{L}(y\log y + (1-y)\log(1-y)), \tag{18}$$

where $L > 0$ is the constant heat of solution.

Chemical potentials. In order to calculate the chemical potentials we construct from the above at first the function $\psi(T, n_{\mathrm{Li}}, n_{\mathrm{V}})$, and then we use (6_1) to obtain

$$\begin{aligned}\frac{1}{L}\mu_{\mathrm{Li}} = {} & f(y) + (1-y)f'(y) + \\ & b_1\left(\log\left(\frac{n_{\mathrm{M}}}{\bar{n}_{\mathrm{M}}h}\right) - \frac{h'}{h}\Big(1 - \frac{\bar{n}_{\mathrm{M}}h}{n_{\mathrm{M}}}\Big)(1-y)\right) + b_2\left(1 - \frac{h'}{h}(1-y)\right)\frac{1}{h},\end{aligned} \tag{19}$$

$$\frac{1}{L}\mu_{\mathrm{V}} = f(y) - yf'(y) + b_1\left(\log\left(\frac{n_{\mathrm{M}}}{\bar{n}_{\mathrm{M}}h}\right) + \frac{h'}{h}\Big(1 - \frac{\bar{n}_{\mathrm{M}}h}{n_{\mathrm{M}}}\Big)y\right) + b_2\left(1 + \frac{h'}{h}y\right)\frac{1}{h}. \tag{20}$$

The newly introduced constants $b_1 = K/(\bar{n}_{\mathrm{M}}L)$ and $b_2 = \bar{p}/(\bar{n}_{\mathrm{M}}L)$ control the strength of mechanical in comparison to chemical contributions.

Voltage of the battery cell in terms of chemical potentials. The simple battery cell that is studied here contains an anode made from metallic lithium.

This fact and the additional assumption that the electrolyte has infinite lithium ion conductivity implies a simple relation between the cell voltage U and the difference $\mu = \mu_{\mathrm{Li}} - \mu_{\mathrm{V}}$ of the involved chemical potentials. It reads

$$U = -\frac{\mu}{e} + U_0 \ , \quad \text{with the useful identity} \quad \mu = \frac{1}{n_{\mathrm{M}}} \frac{\partial \rho \tilde{\psi}}{\partial y} \ . \tag{21}$$

where e denotes the charge of an electron, U_0 is the basic cell voltage, and $(21)_2$ follows from $(6)_2$ by a simple calculation.

3.4 Exploitation of mechanical equilibrium

In comparison with chemical processes, mechanical equilibrium is much faster established, so that it is reasonable to assume that the storage system is in mechanical equilibrium at any time. This assumption implies a large simplification of the available free energy, and we shall thus exploit mechanical equilibrium in advance before we discuss the chemical equilibria in detail.

For each single $FePO_4$ particle with index $l \in 1, 2, .., N$ we have according to (12) and (15)

$$p(y^l, n_{\mathrm{M}}^l) = p_0 \quad \text{implying} \quad K\left(\frac{n_{\mathrm{M}}^l}{\bar{n}_{\mathrm{M}}} - h(y^l)\right) = p_0 - \bar{p}, \tag{22}$$

which gives the function $n_{\mathrm{M}}^l = \hat{n}_{\mathrm{M}}(y^l)$.

4 The many particle system in detail

4.1 Characterization of equilibria

For instantaneous mechanical equilibrium, exploited in 3.4, the available free energy (7) reduces to

$$A(y^1, \ldots, y^{N-1}, q) = \frac{N_{\mathrm{M}}}{N} \sum_{l=1}^{N} \left(\frac{1}{\hat{n}_{\mathrm{M}}^l} \rho^l \tilde{\psi}^l + \frac{p_0}{\hat{n}_{\mathrm{M}}^l}\right) = \frac{N_{\mathrm{M}}}{N} \sum_{l=1}^{N} F(y^l) \tag{23}$$

with the side condition

$$y^N = Nq - \sum_{l=1}^{N-1} y^l \ . \tag{24}$$

The abbreviation $F(y) = \frac{1}{n_{\mathrm{M}}}(\rho\tilde{\psi} + p_0)$ simplifies the further discussion.

The available free energy has a local minimum at any equilibrium point. If the filling degree q is fixed, the necessary conditions for equilibria are now exclusively given by

$$0 = \frac{\partial A}{\partial y^l} = \frac{N_{\mathrm{M}}}{N}\left(\hat{\mu}(y^l) - \hat{\mu}(y^N)\right) \qquad \text{for all} \quad l = 1, \ldots, N-1 \ . \tag{25}$$

Here the chemical potential function $\hat{\mu}$ is given by $\hat{\mu}(y) = \mu(y, \hat{n}_{\mathrm{M}}(y)) = \frac{dF}{dy}$.

According to (21) we conclude from (25) that each particle has the same voltage.

In order to select only solutions of (25) that are equilibria, the Hessian H

$$H_{lk} := \frac{\partial^2 A}{\partial y^l \partial y^k} \quad = \quad \frac{N_{\mathrm{M}}}{N} \left(\frac{\partial \hat{\mu}}{\partial y}\Big|_{y=y^l} \delta_{lk} + \frac{\partial \hat{\mu}}{\partial y}\Big|_{y=y^N} \right) \ . \tag{26}$$

must be positive definite. The Hessian of $A(\cdot, q)$ can also be positiv semi definite, and then further investigations must be made.

The crucial point now is, that the chemical potential $\hat{\mu}$ is a smooth non-monotone function. We assume that F and the chemical potential $\hat{\mu}$ satisfies the assumptions:

(A1) $F \in C^2((0,1);\mathbb{R}) \cap C([0,1];\mathbb{R})$

(A2) There exist $y_*, y^* \in (0,1)$ with $y_* < y^*$, so that $\hat{\mu}$ is strictly decreasing in the interval $[y_*, y^*]$ and strictly increasing else.

(A3) $\lim\limits_{y \searrow 0} \hat{\mu}(y) = -\infty \quad$ and $\quad \lim\limits_{y \nearrow 1} \hat{\mu}(y) = +\infty$.

(A4) $\hat{\mu}'$ is strictly convex.

The assumption (A4) can be replaced by the weaker assumption

(A4') For all $y \in (0,1)$ we have $\mu'(z) = 0 \ \Leftrightarrow z \in \{y_*, y^*\}$.

We only use assumption (A4) to keep the proofs simple. Note that according to $(21)_2$ the chemical potential $\hat{\mu}$ satisfies the assumptions, and its structure is illustrated in Figure 4.

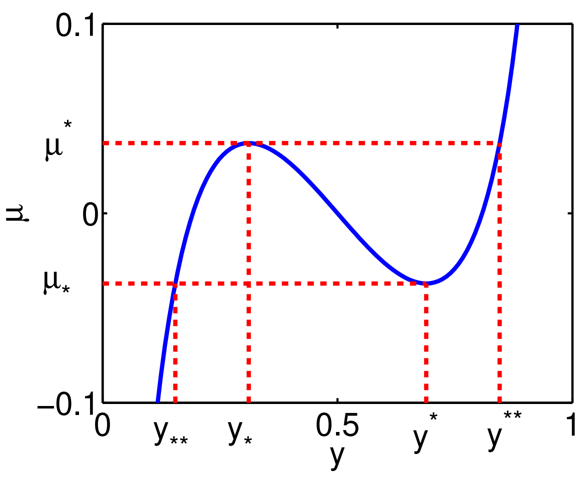

Figure 4: Qualitative description of chemical potential μ

Next we define the set of equilibria on $M_q := \{z \in [0,1]^{N-1} \,|\, 0 \le Nq - \sum_{l=1}^{N-1} z^l \le 1\}$ as

$$\Lambda_q^N := \Big\{ y \in [0,1]^N |\ (y^1, \dots, y^{N-1}) \text{ local minimum of } A(.,q) \text{ on } M_q, \\ y^N = Nq - \sum_{l=1}^{N-1} y^l \quad \text{and} \quad y^i \le y^{i+1} \Big\} . \tag{27}$$

In order to ignore permutations the particles of equilibrium states are sorted according to the mole fractions.

The assumption (A3) implies that no local minimum of $A(\cdot, q)$ lies on the boundary of $[0,1]^N$ for $q \notin \{0;1\}$. Let $q \in (0,1)$ be fixed and $y \in \Lambda_q^N$. Then there must be particle indices $i, j \in \{1, \dots, N\}$ so that $y^i < 1$ and $y^j > 0$. Let us assume, there exists an index $k \in \{1, \dots, N\}$ so that $y^k = 1$. The assumptions (A1),(A3) imply that the function $f \in C^1((0,\delta);\mathbb{R}) \cap C([0,\delta];\mathbb{R})$, defined by

$$f(\varepsilon) := F(y^i + \varepsilon) + F(y^k - \varepsilon) \qquad \text{for} \quad \varepsilon \in [0,\delta] , \tag{28}$$

is strictly monotone decreasing on $[0,\delta]$, where $\delta > 0$ is sufficiently small. Therefore the state $\tilde{y}_\varepsilon$

$$\tilde{y}_\varepsilon^l := \begin{cases} y^i + \varepsilon & \text{if } l = i \\ y^k - \varepsilon & \text{if } l = k \\ y^l & \text{otherwise} \end{cases} \qquad \text{for } l = 1, \dots, N . \tag{29}$$

satisfies the side condition (24), and using (28) we obtain

$$A(\tilde{y}_\varepsilon^1, \dots, \tilde{y}_\varepsilon^{N-1}, q) < A(y^1, \dots, y^{N-1}, q) \qquad \text{for all} \quad \varepsilon \in (0, \delta] \tag{30}$$

This contradicts the assumption that y is a local minimum of A on M_q. The case of an index k with $y^k = 0$ can be excluded by a similar reasoning. It follows, that the set of equilibria reduce to

$$\Lambda_q^N = \Big\{ y \in (0,1)^N |\ (y^1, \dots, y^{N-1}) \text{ local minimum of } A(.,q) \text{ on } M_q, \\ y^N = Nq + \sum_{l=1}^{N-1} y^l \quad \text{and} \quad y^i \le y^{i+1} \Big\} , \tag{31}$$

and for each equilibrium state $y \in \Lambda_q^N$, there must hold the necessary condition (25).

In the case $q \in (0, y_{**}] \cup [y^{**}, 1)$, see Figure 4, the set of equilibria reduces to

$$\Lambda_q^N = \Big\{ y \in (0,1)^N |\ y^l = q \text{ for all } l = 1, \dots, N \Big\} . \tag{32}$$

A crucial behavior of the many particle system is described by the following lemma.

Lemma 1. *Let $q \in (0,1)$ be fixed.*

1. Based on the assumptions (A1)-(A4), there exists a sequence $\{\delta_N\}_{N\in\mathbb{N}}$ with $\lim\limits_{N\to\infty}\delta_N = 0$ so that for all $N \in \mathbb{N}$:

$$y^l \in (0, y_* + \delta_N) \cup (y^* - \delta_N, 1) \quad \textit{for all} \quad y = (y^1, \dots, y^N) \in \Lambda_q^N \ . \tag{33}$$

2. Furthermore at most one mole fraction is in the intermediate region (y_*, y^*).

Proof. The case $q \in (0, y_{**}] \cup [y^{**}, 1)$ is trivial due to the characterization (32).

We denote by $e_i \in \mathbb{R}^{N-1}$ the i-th unit vector, which has an entry 1 at the i-th position and zero entries otherwise.

Let $q \in (y_{**}, y^{**})$ and $N \in \mathbb{N}$. For any $y = (y^1, \dots, y^N) \in \Lambda_q^N$ the equations (24), (25) imply $y^l \in [y_{**}, y^{**}]$ $(l = 1, \dots, N)$ and it follows from the continuity

$$|\hat{\mu}'(y)| \le c_0 \quad \text{for all} \quad y \in \Lambda_q^N \ . \tag{34}$$

Let $l_* \in \{1, \dots, N)$ and $y^{l_*} \in (y_*, y^*)$, which implies $\hat{\mu}'(y^{l_*}) \le 0$. Next, we define

(a) if $l_* < N$, $x := e_{l_*} - \frac{1}{N-1}\sum_{i=1, i\ne l_*}^{N-1} e_i$,

(b) if $l_* = N$, $x := \frac{1}{N-1}\sum_{i=1}^{N-1} e_i$.

In both cases, we conclude from the Hessian (26)

$$0 \le x^T H(y) x = \hat{\mu}'(y^{l_*}) + \frac{1}{(N-1)^2}\sum_{i=1, i\ne l_*}^{N-1} \hat{\mu}'(y^i) \ . \tag{35}$$

Thus due to (34) we have

$$0 \le |\hat{\mu}'(y^{l_*})| \le \frac{\frac{1}{N-1}\sum_{i=1, i\ne l_*}^{N-1} \hat{\mu}'(y^i)}{N-1} \le \frac{c_0}{N-1} \ . \tag{36}$$

This means for sufficiently large N, that $\hat{\mu}'(y^{l_*})$ is close to zero. The strict convexity of μ' implies that there exist only two values $y_N^1 < y_N^2$ (N sufficiently large) with

$$\hat{\mu}'(y_N^1) = \hat{\mu}'(y_N^2) = -\frac{c_0}{N-1} \ . \tag{37}$$

From $\hat{\mu}(y_*) = \hat{\mu}(y^*) = 0$ follows $y_* < y_N^1 < y_N^2 < y^*$ and $y^{l_*} \in (y_*, y_N^1] \cup [y_N^2, y^*)$. The convexity of μ' also implies $y_N^1 > y_{N+1}^1$, $y_N^2 < y_{N+1}^2$ and we define $\delta_N := \max\{|y_N^1 - y_*|, |y^* - y_N^2|\}$ so that the assertion holds.

Next we prove that only one mole fraction $y^j \in \Lambda_q^N$ for $j \in 1, ..., N$ is in the intermediate region (y_*, y^*). The case $q \in (0, y_{**}] \cup [y^{**}, 1)$ is trivial. Let $q \in (y_{**}, y^{**})$ and $y^l, y^k \in (y_*, y^*)$, this implies $\hat{\mu}'(y^l), \hat{\mu}'(y^k) < 0$ and

(a) if $k, l < N$ define $x := e_k - e_l$ then we have $x^T H(y) x < 0$

(b) if $l < N, k = N$ define $x := e_l$ then we have $x^T H(y)x < 0$

so that that we do not have a minimum for two mole fractions $y^l, y^N \in (y_*, y^*)$. □

The lemma shows, that the individual storage particles of a many particle system may not behave identical. In equilibrium they may form two phases, denoted by α- and β-phase, with mole fractions in $(0, y_* + \delta_N)$, respectively in $(y^* - \delta_N, 1)$. For $y = (y^1, \ldots, y^N) \in \Lambda_q^N$ the lemma implies the existence of a unique number M of particles in the β-phase. This leads to the following definition.

Definition 1. *For given $y \in \Lambda_q^N$ we define the fraction of particles in the β-phase*

$$\hat{\lambda}(y) := \frac{M}{N}. \tag{38}$$

We may say that λ describes an internal state of the many particle system, whereas its macroscopic state is characterized by the filling degree q.

A system state that satisfies (25) and (24) attains the same chemical potential $\hat{\mu}$ for all particles. This allows to plot each system state in a (μ, q)-diagram, see Figure 5. Therefore we write for all $y = (y^1, \ldots, y^N) \in (0,1)^N$ that satisfy (24) and (25).

$$\hat{\mu}(y) \ := \ \hat{\mu}(y^1) = \cdots = \hat{\mu}(y^N) \ . \tag{39}$$

The last lemma shows, that at most one particle has a mole fraction y^{l_*} in the intermediate region (y_*, y^*) and for large N we have y^{l_*} either close to y_* or to y^*. We are exclusively interested in systems with many storage particles, so that from now on we will ignore equilibria with individual particles in the region (y_*, y^*). This fact motivates the following model assumption:

(A5) There is no index $k \in \{1, 2, ..., N\}$ so that the mole fraction y^k is in the intermediate region (y_*, y^*).

Thus from now on we consider equilibria that are contained in the set

$$\tilde{\Lambda}_q^N := \{y \in \Lambda_q^N \mid y \text{ satisfies (A5)}\} \ . \tag{40}$$

Figure 6 shows the equilibria for 10 and for 30 particles under the assumption (A5) in (μ, q)-plot.

We revisit now Figures 5 and 6 and observe that the points indicating equilibria separate into different branches for increasing N. Later on, we shall show that equilibrium points of the same branch have the same internal state $\lambda \in \{0, 1/N, \ldots, 1\}$. Therefore, for a fixed $\lambda \in \{0, 1/N, \ldots, 1\}$ we call the set

$$B_\lambda := \{y \in (0,1)^N \,|\exists q \in (0,1) : y \in \tilde{\Lambda}_q^N \text{ with } \hat{\lambda}(y) = \lambda\} \tag{41}$$

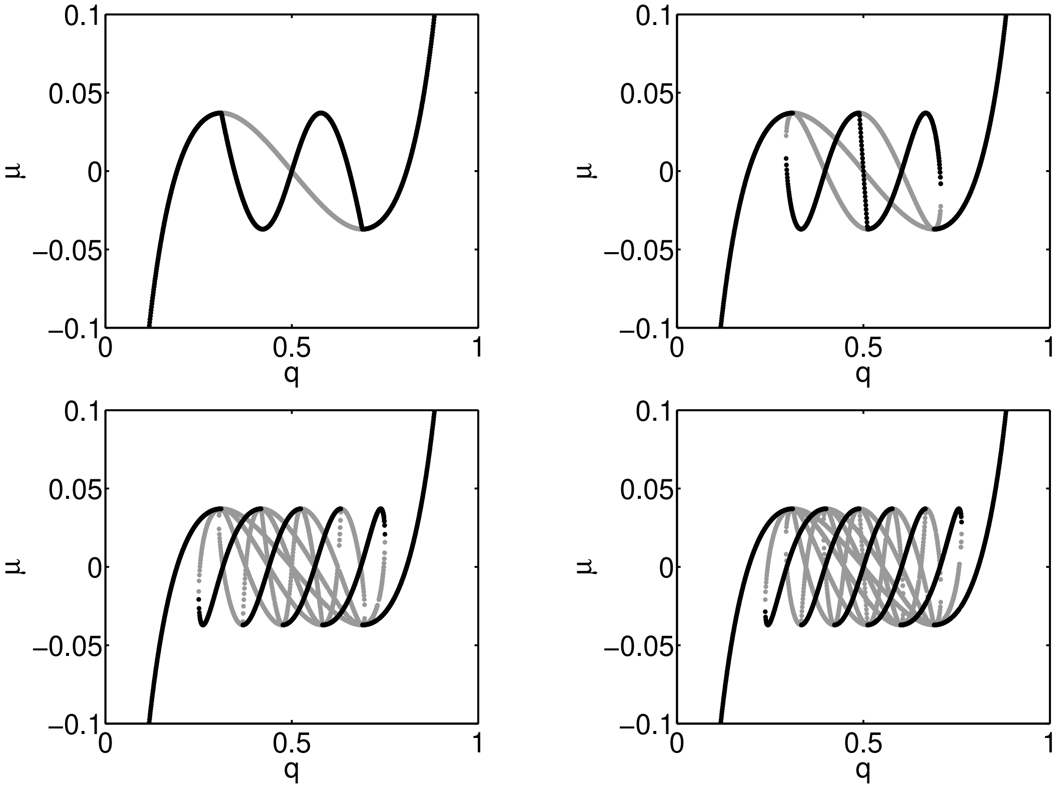

Figure 5: Chemical potentials for system states $y \in (0,1)^N$ that satisfies (24) and (25) for 2, 3, 5 and 6 particles. The equilibria are indicated by the black color.

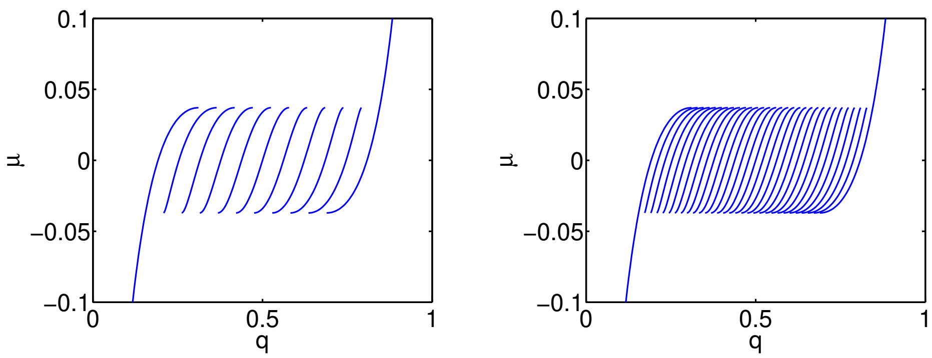

Figure 6: Chemical potentials for equilibria satisfying assumption (A5). Left: 10 storage particles, right: 30 storage particles.

a branch of equilibrium states. In other words B_λ contains those equilibria that have the same number of particles in the β-phase.

Exploitation of the necessary conditions (25) for equilibria yields: The mole fractions $y = (y^1, \dots, y^N) \in \tilde{\Lambda}_q^N$ of the storage particles can assume only two values with low and high mole fraction, which are indicated by Y^- respectively Y^+. The side condition (24) can then be written as $q = \hat{\lambda}(y)Y^+ + (1-\hat{\lambda}(y))Y^-$, and Assumption (A5) implies $Y^- \leq y_*$ and $Y^+ \geq y^*$. The next lemma proves existence and uniqueness of the pair $Y^\pm$ and their continuous dependence on the filling degree q.

The continuity yields that the branches B_λ define connected sets in $(0,1)^N$.

Lemma 2. *Let $\lambda \in \{1/N, 2/N, \dots, (N-1)/N\}$ be fixed and assume that (A1)-(A3) are satisfied. We define the interval $Q_\lambda := \big(q_\lambda^-, q_\lambda^+\big)$ with $q_\lambda^- := \lambda y^* + (1-\lambda)y_{**}$ and $q_\lambda^+ := \lambda y^{**} + (1-\lambda)y_*$. There exist unique functions*

$$Y_\lambda^- \in C(Q_\lambda, (y_{**}, y_*)) \quad \textit{and} \quad Y_\lambda^+ \in C(Q_\lambda, (y^*, y^{**})) \ , \tag{42}$$

which satisfy

$$\begin{aligned} q &= \lambda Y_\lambda^+(q) + (1-\lambda)Y_\lambda^-(q) && (43) \\ \hat{\mu}(Y_\lambda^+(q)) &= \hat{\mu}(Y_\lambda^-(q)) && (44) \end{aligned}$$

for all $q \in Q_\lambda$.

Proof. In order to show the existence, we define the functions

$$\begin{aligned} g_0 &: (\mu_*, \mu^*) \to (y_{**}, y_*) & g_0 &:= \big(\hat{\mu}|_{(y_{**}, y_*)}\big)^{-1} && (45) \\ g_1 &: (\mu_*, \mu^*) \to (y^*, y^{**}) & g_1 &:= \big(\hat{\mu}|_{(y^*, y^{**})}\big)^{-1} && (46) \end{aligned}$$

which are the inverses of the two monotone increasing branches of $\hat{\mu}$ and furthermore we define

$$g_\lambda : (\mu_*, \mu^*) \to (y_{**}, y^{**}) \qquad g_\lambda := \lambda g_1 + (1-\lambda) g_0. \tag{47}$$

Recall that the functions $g_{0,1}$ are strictly monotone increasing and this implies g_λ is strictly monotone increasing. Therefor $g_\lambda(\mu_*, \mu^*) = Q_\lambda$ and the function

$$\mu_\lambda := g_\lambda^{-1} \tag{48}$$

is well defined and continuous on Q_λ. Now we define y_λ^-, y_λ^+ as

$$y_\lambda^-(q) := g_0(\mu_\lambda(q)) \qquad y_\lambda^+ := g_1(\mu_\lambda(q)) \ , \tag{49}$$

which are continuous and defined on Q_λ. Note that (43) and (44) are valid by construction.

The uniqueness directly follows from (43) and (44). If we solve equation (43) for y^- and insert the result into (44), we may define

$$G(y^+) := \hat{\mu}(y_\lambda^+) - \hat{\mu}\Big(\frac{q - \lambda y_\lambda^+}{1-\lambda}\Big) \ . \tag{50}$$

The function G is strictly monotone, so that its root y_λ^+ is unique. □

Remark 1. *We conclude from Lemma 2 that we can construct, for fixed $\lambda \in \{0, 1/N, \ldots, (N-1)/N, 1\}$, continuous mole fractions y_λ of the filling degree $q \in Q_\lambda$ with values in $\tilde{\Lambda}_q^N$.*

$$y_\lambda^i(q) := \begin{cases} Y_\lambda^-(q) & i \leq (1-\lambda)N \\ Y_\lambda^+(q) & i > (1-\lambda)N \end{cases} \tag{51}$$

so that $y_\lambda(q) \in \tilde{\Lambda}_q^N$ for all $q \in Q_\lambda$.

In the case $\lambda \in \{1/N, \ldots, (N-1)/N\}$ the functions Y_λ^-, Y_λ^+ and the set Q_λ are defined in Lemma 2.

In the case $\lambda \in \{0, 1\}$ the functions are defined as $Y_\lambda^+(q) = Y_\lambda^-(q) := q$ for $q \in Q_\lambda$, where $Q_0 := (0, y_*)$ and $Q_1 := (y_*, 1)$.

The functions $y_\lambda^\pm$ are continuously expandable to $\overline{Q}_\lambda$.

Remark 2. *For each equilibrium state of $\tilde{\Lambda}_q^N$ there exists Y^- and Y^+ which satisfy (43),(44) and as a result of the uniqueness in Lemma 2 every equilibrium state belonging to $\tilde{\Lambda}_q^N$ can be reached by a function y_λ.*

As a consequence we have

$$\overline{B}_\lambda = \{y_\lambda(q) | q \in \overline{Q}_\lambda\} \qquad \lambda \in \{0, 1/N, \ldots, 1\} . \tag{52}$$

This means that each branch B_λ can be characterized by the function y_λ, and each branch in the (μ, q) plot, see Figure 6, is defined by $\{\hat{\mu}(y_\lambda(q)) \mid q \in \bar{Q}_\lambda\}$.

At last, we state that the vertical distance between the chemical potential of two branches in the (μ, q)-plot decreases if the number of storage particles increases. This fact can be observed in Figure 6 and additionally follows from the following corollary.

Corollary 1. *Let $y_\lambda \in C(\overline{Q}_\lambda; (0,1)^N)$ be defined as in Remark 1. For $\varepsilon > 0$ exists a number$N^* \in \mathbb{N}$ so that*

$$\max_{q \in \overline{Q}_\lambda \cap \overline{Q}_{\lambda+1/N}} |\hat{\mu}(y_\lambda(q)) - \hat{\mu}(y_{\lambda+1/N}(q))| \leq \varepsilon \tag{53}$$

for all $N \geq N^*$ and for all $\lambda \in \{0, 1/N, \ldots, (N-1)/N\}$.

Proof. Let $\lambda \in \{0, 1/N, \ldots, (N-1)/N\}$ and $q \in \overline{Q}_\lambda \cap \overline{Q}_{\lambda+1/N}$. The functions y_λ and $y_{\lambda+1/N}$ are continuous so that the maximum is well defined on the closed set $\overline{Q}_\lambda \cap \overline{Q}_{\lambda+1/N}$.

In the following we ignore the argument q in y_λ and $y_{\lambda+1/N}$.

The functions y_λ satisfy identity (43) and it therefor follows for $q \in \overline{Q}_\lambda \cap \overline{Q}_{\lambda+1/N}$

$$(1-\lambda)\left(y_\lambda^- - y_{\lambda+1/N}^-\right) + \lambda\left(y_\lambda^+ - y_{\lambda+1/N}^+\right) = \frac{1}{N}\left(y_{\lambda+1/N}^+ - y_{\lambda+1/N}^-\right) \tag{54}$$

and from identity (44) they satisfy

$$\hat{\mu}(y_\lambda^-) = \hat{\mu}(y_\lambda^+) \qquad \text{and} \qquad \hat{\mu}(y_{\lambda+1/N}^-) = \hat{\mu}(y_{\lambda+1/N}^+) \ . \tag{55}$$

$q \in \overline{Q}_\lambda \cap \overline{Q}_{\lambda+1/N}$ implies that $y_{\lambda+1/N}^- \leq y_*$ and $y_{\lambda+1/N}^+ \geq y^*$, and furthermore with (54) we conclude

$$(1-\lambda)\left(y_\lambda^- - y_{\lambda+1/N}^-\right) + \lambda\left(y_\lambda^+ - y_{\lambda+1/N}^+\right) \geq \frac{1}{N}\left(y^* - y_*\right) > 0 \ . \tag{56}$$

The monotonicity of $\hat{\mu}$ implies via (55) and (56)

$$y_\lambda^+ - y_{\lambda+1/N}^+ \geq 0 \qquad \text{and} \qquad y_\lambda^- - y_{\lambda+1/N}^- \geq 0 \ . \tag{57}$$

Note, if $q \in \overline{Q}_\lambda \cap \overline{Q}_{\lambda+1/N}$ then $y_{\lambda+1/N}^+, y_{\lambda+1/N}^- \in [y_{**}, y^{**}]$, and from (54) we obtain

$$\begin{aligned} &\min\{|y_\lambda^- - y_{\lambda+1/N}^-|, |y_\lambda^+ - y_{\lambda+1/N}^+|\} \\ \leq &(1-\lambda)\left(y_\lambda^- - y_{\lambda+1/N}^-\right) + \lambda\left(y_\lambda^+ - y_{\lambda+1/N}^+\right) \\ \leq &\frac{1}{N}(y^{**} - y_{**}) \ . \end{aligned} \tag{58}$$

Finally the boundedness of $\hat{\mu}$ on $[y_{**}, y^{**}]$ and (55) implies

$$|\hat{\mu}(y_\lambda) - \hat{\mu}(y_{\lambda+1/N})| = |\hat{\mu}(y_\lambda^+) - \hat{\mu}(y_{\lambda+1/N}^+)| = |\hat{\mu}(y_\lambda^-) - \hat{\mu}(y_{\lambda+1/N}^-)| \tag{59}$$

$$\leq c_0 \min\{|y_\lambda^- - y_{\lambda+1/N}^-|, |y_\lambda^+ - y_{\lambda+1/N}^+|\} \tag{60}$$

$$\leq \frac{c_0}{N}(y^{**} - y_{**}) \ . \tag{61}$$

□

4.2 Quasi-static evolution

Up to now we have studied the behavior of the storage system for constant filling degree q. In this section we assume that the filling degree q slowly depends on time and therefore we study now a quasi-static evolution of the system. Thus during the time interval $I = [t_0, t_1]$ its evolution $y : I \to (0,1)^N$ must satisfy $y(t) \in \tilde{\Lambda}_{q(t)}^N$ for all $t \in I$.

At first we discuss the expected behavior. To this end we start from an equilibrium state $y_0 \in \tilde{\Lambda}_q^N$ with $q \in (0,1)$. Then Lemma 1 implies, that the storage particles are separated in α- and β-phase, with corresponding mole fractions Y^-, respectively Y^+. If the process is sufficiently slow, so that $|\dot{q}| \ll 1$, then we expect that the system does not change significantly, i.e. $|y(t_0) - y(t_0 + \varepsilon)| \ll 1$, and we expect the evolution of the mole fractions $y = (y^1, ..., y^N)$ to be continuous.

Corollary 2. *Let $I = [t_0, t_1]$ be a time interval, $y_0 \in \tilde{\Lambda}^N_{q_0}$ with phase fraction $\hat{\lambda}(y_0)$ and $q \in C(I; Q_\lambda)$ with $q_0 = q(t_0)$. Then there exists a unique continuous function $y : I \to (0,1)^N$ satisfying*

$$y(t_0) = y_0 \qquad \text{and} \qquad y(t) \in \tilde{\Lambda}^N_{q(t)} \quad \text{for all} \quad t \in I. \tag{62}$$

Proof. We conclude from Remark 1 that the function $y(\cdot) := y_{\hat{\lambda}(y_0)}(q(\cdot))$ is continuous and we have $y(t) \in \tilde{\Lambda}^N_{q(t)}$ for all $t \in I$. Let us now assume, that there exist mole fractions $\bar{y} \in C(I; (0,1)^N)$ with $\bar{y}(t) \in \tilde{\Lambda}^N_{q(t)}$ and $\bar{y}(t_0) = y_0$. Starting from the initial value and applying the continuity property yields that for all $t \in I$ the function $\bar{y}$ has the same phase fraction $\hat{\lambda}(y_0)$. The uniqueness follows from Lemma 2. □

So far we could describe the behavior of the system as long as the filling degree q stays in an open set Q_λ during the considered time interval.

Now we pose the question, what happens if q runs over the boundary of $Q_\lambda = (q^-_\lambda, q^+_\lambda)$. For simplicity we only discuss the case where q is increasing in time and exceeds $q^+_\lambda = q(t_*)$ at a certain time t_*. By assuming continuous (in time) mole fractions $y(t) = y^1(t), ..., y^N(t)$, one can uniquely determine the state $y(t_*)$. The positive definiteness of the Hessian matrix and therefore the requirement that the system runs through equilibria is not guaranteed at this limit state. However for $q(t) > q^+_\lambda$ it is possible to continue the state y such that we have the necessary condition (25) for equilibrium with the phase fraction $\hat{\lambda}(y(t_0))$, though the extension do not minimize the energy A. For this reason we call the state that results for $q(t_*)$ a critical point.

Obviously within the setting of quasi-static evolution we need a further model assumption in order to describe how the storage particle system evolves if q exceeds q^+_λ. Motivated by an analogy with N interconnected rubber balloons, where we observe a similar behavior, we state that the system state changes discontinuously. An α-phase particle changes at q^+_λ to the β-phase and the phase fraction $\hat{\lambda}(y(t))$ accordingly changes to $\hat{\lambda}(y(t_* + \varepsilon)) = \hat{\lambda}(y(t_*)) + 1/N$ for ε small enough.

This behavior is represented in the (μ, q)-plot as follows. During the evolution, the particle system follows the branch B_λ to its end, i.e. up to the critical point $q(t_*)$, and then drops to the next branch $B_{\lambda+\frac{1}{N}}$ if q exceeds $q(t_*)$. Note that for sufficiently large N for $\lambda \in \{0, 1/N, \ldots, 1\}$ we have

$$q^+_\lambda \in \overline{Q}_\lambda \cap \overline{Q}_{\lambda+1/N} \quad \text{for } \lambda < 1 \ , \qquad q^-_\lambda \in \overline{Q}_\lambda \cap \overline{Q}_{\lambda-1/N} \quad \text{for } \lambda > 0, \tag{63}$$

so that the above described behavior is allowed within the quasi-static setting.

Now we summarize the assumed behavior of the storage particle system in a slightly more systematic way. Recall that the evolution $I := [t_0, t_1] \to (0,1)^N$ of the state y depends on the filling degree $q \in C(I; (0,1))$ and on the initial value $y_0 \in \tilde{\Lambda}^N_{q(t_0)}$.

(A5) (i) The evolution starts from y_0 with phase fraction $\hat{\lambda}(y_0)$ and $q(t_0) \in Q_{\hat{\lambda}(y_0)}$.

(ii) The evolution evolves along the function $y(t) = y_{\hat{\lambda}(y_0)}(q(t))$, with $y(t_0) = y_0$, where $y_{\hat{\lambda}(y_0)}$ is defined in Remark 1, until the system reaches a critical state where either $q(t_*) = q^-_{\hat{\lambda}(y_0)}$ or $q(t_*) = q^+_{\hat{\lambda}(y_0)}$.

(iii) If

$$\begin{cases} q(t_*) = q^-_{\hat{\lambda}(y_0)} & \text{then } y(t_*) := y_{\hat{\lambda}(y_0)-1/N}(q(t_*)) \\ q(t_*) = q^+_{\hat{\lambda}(y_0)} & \text{then } y(t_*) := y_{\hat{\lambda}(y_0)+1/N}(q(t_*)) \end{cases}$$

where the functions $y_{\hat{\lambda}(y_0)-1/N}$ and $y_{\hat{\lambda}(y_0)+1/N}$ are defined in Remark 1.

(iv) The evolution proceeds at (i) with $t_0 = t_*$ and $y_0 = y(t_*)$.

The Corollary 2 guarantees that the evolution of the mole fractions y according to assumption (A5) is well defined and unique. Furthermore the construction (A5) implies that the evolution is piecewise continuous. The discontinuities (jumps) are attributed to the passage of a storage particle from the α- to the β-phase or vice versa, see $(A5)_{(iii)}$.

4.3 Asymptotic behavior and hysteresis

In this section we discuss the asymptotic behavior that is induced by the quasi-static evolution of the storage particle system. In particular we will demonstrate that the introduced model is capable to predict the observed hysteretic behavior during charging and discharging of a lithium-ion battery. We start from a fully charged state and consider the process $q : [t_0, t_1] \to (0, 1)$ along the paths

$$q(t) = \begin{cases} \frac{t-t_0}{t_1-t_0} & \text{for } t < \frac{t_0+t_1}{2} \quad \text{(discharging)} \\ \frac{t_1-t}{t_1-t_0} & \text{for } t \geq \frac{t_0+t_1}{2} \quad \text{(charging)} \end{cases} \qquad \text{for} \quad t \in [t_0, t_1] \; . \tag{64}$$

The response of the storage system can at best be described in the plot that gives the chemical potential $\hat{\mu}$ versus the filling degree q of the storage system. Recall, that $-\hat{\mu}$ is proportional to the voltage and $1 - q$ is related to the capacity of the battery, i.e. to the stored electric charge. The Figure 7 shows the response of a storage system with 5 respectively with 10 storage particles.

We observe a path dependence during discharging and charging and moreover, for an increasing number of storage particles occurs a hysteresis loop. This fact is the content of the next corollary, whereupon the jumps of the chemical potential decrease for increasing number of storage particles. For 1000 particles, see Figure 8, they are not visible anymore.

Corollary 3. *Let $q \in C(I; (0, 1))$ and y_N the solution of the quasi static model which satisfies (A5) for $N \in \mathbb{N}$. For $\varepsilon > 0$ exists a number $N_* \in \mathbb{N}$, which depends on ε, so that*

$$\max_{t\in I} | \lim_{s\nearrow t} \hat{\mu}(y_N(s)) - \lim_{s\searrow t} \hat{\mu}(y_N(s))| < \varepsilon \qquad \textit{for all} \quad N > N_* \; . \tag{65}$$

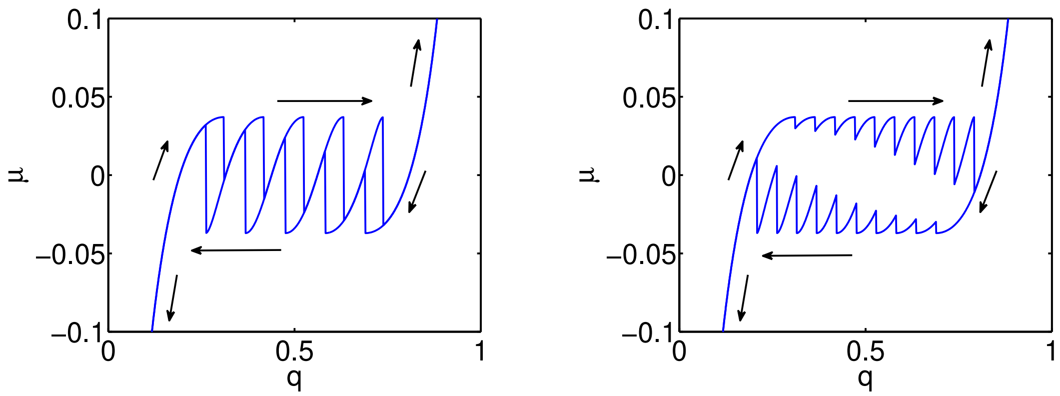

Figure 7: Hysteretic behavior generated by a cathode with 5 (left) and 10 (right) storage particles.

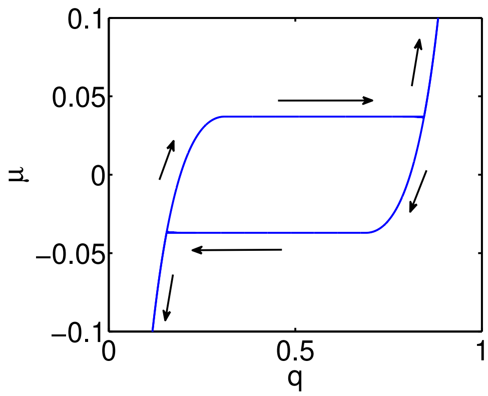

Figure 8: Hysteretic behavior generated by a cathode with 1000 storage particles.

Proof. The model implies that the solution y_N for any N is piecewise continuous. It is only discontinuous if one particle changes the phase. According to Corollary 1 the jumps of $\hat{\mu}$ decrease uniformly for increasing N. □

4.4 Some selected properties of the model

Path dependence. A characteristic observation in lithium-ion batteries concerns the fact that the voltage of a certain charge state depends on the charging history [16]. In order to demonstrate that this path dependence can be explained within the model we consider the following experiment:

1. We fully charge a discharged battery, i.e. we start with $q = 1$ and end up with $q = 0$. The resulting path is indicated in Figure 9_{left} by the red arrows.
2. We discharge now the fully charged battery from $q = 0$ and stop at $q = 0.5$.
3. From here we fully charge the battery down to $q = 0$. The resulting path is indicated in Figure 9_{left} by the blue arrows.

We observe in this experiment that the history, how a given charge state of the battery is reached, is essential in order to predict its subsequent behavior during further charging or discharging. The origin of this phenomenon is easily explained within the setting of the proposed model. The system evolves along different paths, because the number of particles in the β-phase is different for the two charging processes.

Likewise the model predicts the occurrence of an inner hysteretic loop, as it is represented in Figure 9_{right}. The corresponding process is

1. We start with a discharged battery at $q = 1$.
2. Then we charge down to $q = 0.65$.
3. Starting here we discharge and stop at $q = 0.35$.
4. Starting here we fully charge the battery to end up with $q = 0$.

The traversed path is indicated by the blue arrows in Figure 9_{right}.

Mechanical interaction of storage particles. Up to now the discussion relies on the assumption that each storage particle is subjected to the constant outer pressure p_0. Now we take into account that the volume of the particles changes, as it is described in Sections 3.3 and 3.4, leads to an elastic response of the electrolyte. In this case the outer pressure p_0 is no longer a constant but will now become a function of the filling degree q.

Recall the simple constitutive law for the pressure inside a storage particle from Section 3.3. In an analogous manner we assume that the pressure within the electrolyte

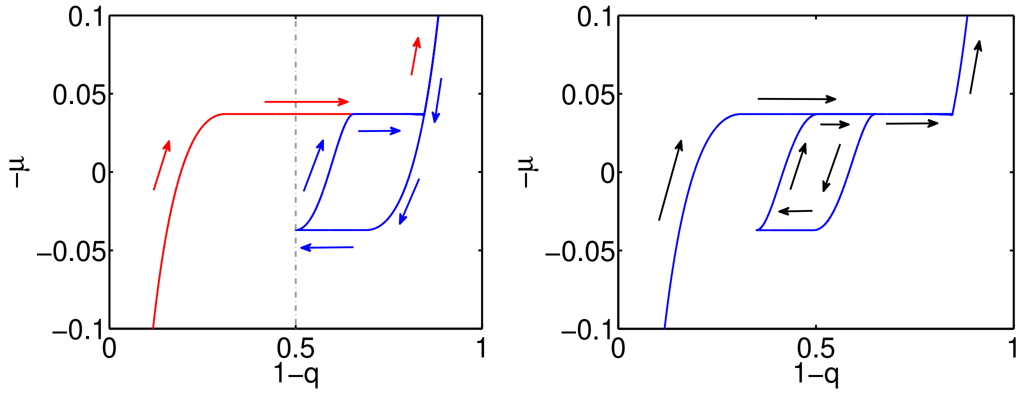

Figure 9: Path-dependence and hysteretic behavior generated by a cathode with 1000 storage particles. Left and right: Different experiments, see text for the details.

is given by a similar law. We write

$$p_0 = p_{\mathrm{R}} + K_{\mathrm{E}} \left(\frac{V_{\mathrm{E}}^0}{V_{\mathrm{E}}} - 1 \right) , \tag{66}$$

where K_{E} is the bulk modulus of the electrolyte and V_{E} is its actual volume which is related to the reference volume V_{E}^0 according to $V_{\mathrm{E}} = V_{\mathrm{E}}^0(1 - \delta q)$. Thus we have

$$p_0 = p_{\mathrm{R}} + K_{\mathrm{E}} \left(\frac{q}{1 - \delta q} \right) . \tag{67}$$

The further treatment of this case is the same as before, i.e. we evaluate the condition of mechanical equilibrium and determine a new function $n_{\mathrm{M}}^l = \hat{n}_{\mathrm{M}}(y^l, q)$ to construct the chemical potentials $\hat{\mu}^l$ of the particles indexed by l. The previous horizontal plateaus, which indicate the 2-phase region in the μ, q diagram now occur with a certain slope as it is shown in Figure 10.

5 An illustrative analogy: Simultaneous inflation of interconnected rubber balloons

We consider N interconnected spherical rubber balloons indexed by $l \in 1, 2, ..., N$ as indicated in Figure 12. Via the pressure vessel the balloons can be simultaneously inflated by air.

The pressure difference $p^l - p_0$ of each balloon with respect to the outer pressure p_0, is related to its actual radius r by

$$p^l - p_0 = \alpha \left(\frac{R}{r^l} - \left(\frac{R}{r^l} \right)^7 \right) \left(1 + \beta \left(\frac{r^l}{R} \right)^2 \right) , \tag{68}$$

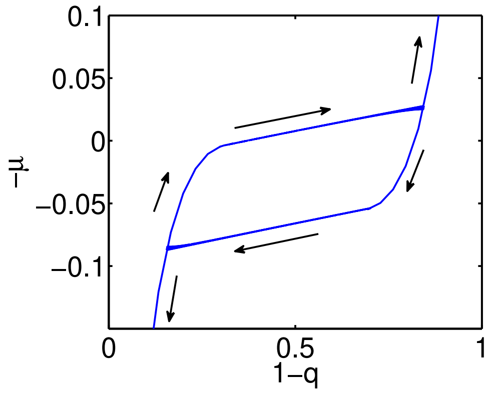

Figure 10: Storage system with 250 particles. Due to mechanical interactions the previous horizontal 2-phase plateaus achieve a slope.

where R is the radius of the undeformed balloon and $\alpha > 0$ and $\beta > 0$ are related to the initial thickness of the balloon and to the elastic constants of rubber, more details are found in [6] and [13]. The function (68) is represented in Figure 11 and

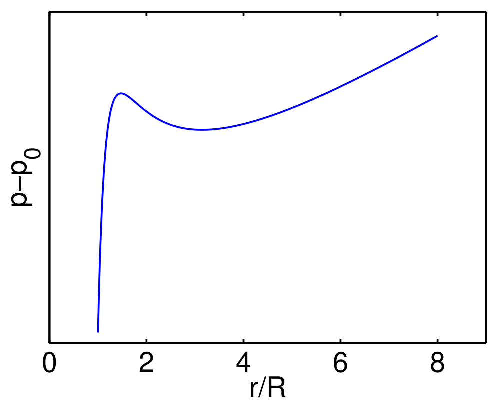

Figure 11: Non-monotone pressure-radius relation of a spherical elastic rubber balloon

shows a non-monotone graph, which qualitatively induces the same behavior as the chemical potentials of the storage particles from above, compare with Figure 4.

In case that a single balloon is inflated by supply of air under fixed pressure, the decreasing part of the pressure-radius relation is an unstable branch.

Now we consider the process that is illustrated by Figure 12. There is a constant supply of air into the pressure vessel and that air freely distributes among the balloons. The following happens: As long as the filling of balloons is small, they all have the same size until they reach with increasing filling the end of the first increasing pressure-radius branch. Careful observation now reveals that only one balloon will pass quickly through the decreasing branch to an apparent larger radius,

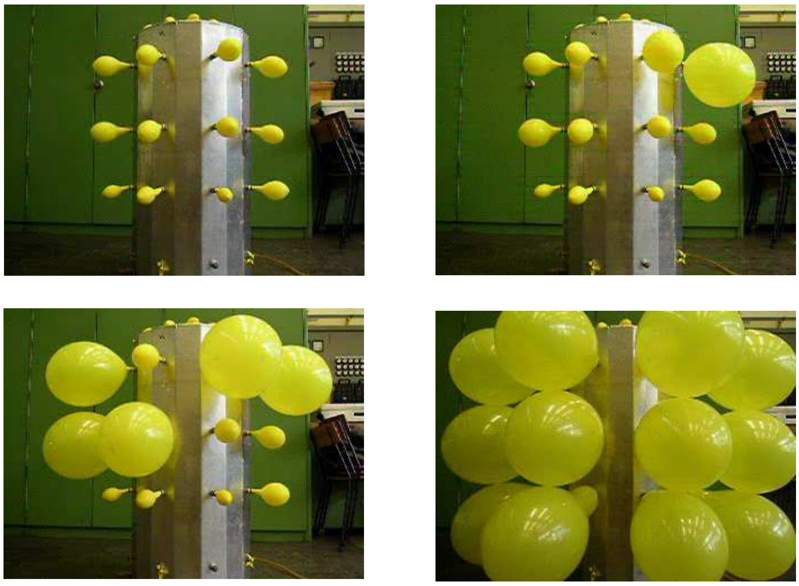

Figure 12: Four different states of connected rubber balloons during loading with air via the pressure vessel.

whereas the other balloons slightly decrease at first their radii before all balloons again increase their radii due to the constant supply of air. In that time regime we thus have one large balloon and $N-1$ small ones. This regimes ends when the small balloons again reach the end of the first increasing pressure-radius branch, and here the same event as before happens. One balloon passes to a larger radius, whereas now $N-2$ balloons slightly fall back, and we have now a state with 2 large balloons and $N-2$ small ones. This process is repeated until all balloons have the same large size, which is the last state of the sequence from Figure 12.

The interpretation and in particular the analogy to the behavior of the many storage particle system from above is obvious. There is a regime of two coexisting phases, formed by small respectively large balloons. Each balloon is a homogeneous and single phase object, however, some balloons are in one phase and the others are in the other phase. See [8], [9] and [13] for more details. The same happens in the storage system during charging and discharging of the battery: There is a regime of particles with small respectively large lithium content. Each storage particle is a homogeneous and single phase object, however, some particles are in one phase and the others are in the other phase.

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