A simple model for charge storage in a nanotube

Wolfgang Schmickler [1]

Institute of Theoretical Chemistry, Ulm University D-89069 Ulm, Germany

ARTICLE INFO

ABSTRACT

We consider a narrow nanotube in contact with an ionic liquid; the sizes of the ions are supposed to be so different that only one kind of ion can enter the tube. For a given number of N equal ions in the tube, the distance between the ions is determined by Coulomb repulsion. Using results obtained previously from density functional theory, we calculate the energy of an ensemble of equal ions, including vibrations about the equilibrium positions. For large tubes, in the thermodynamic limit, the resulting capacity diverges at zero charge for entropic reasons. It then increases rapidly, passes through a maximum, and becomes smaller as the distance between the ions decreases with increasing charge. Small nanotubes exhibit discrete charging steps reminiscent of quantum dots.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The electrochemical storage of ions in nanotubes is of great practical and theoretical interest. Nanotubes are an excellent electrode material for supercapacitors [1,2]; at the same time, the confinement of an electrolyte in such narrow spaces offers various challenges to theory. The diameter of small tubes is smaller than the typical extension of the electric double layer at planar electrodes, which requires new models for the distribution of particles and charges in these confined spaces. A clear indication of new phenomena in very small nanotubes was the experimental finding [3,4] that nanotubes, which are so small that the fully solvated ions cannot enter, store energy more efficiently than wider tubes. This led Kondrat and Kornyshev [5] to postulate a superionic state for ions in very narrow pores, where the interaction between the ions as strongly screened by the image charges on the wall, which allows a denser packing of ions of the same charge. They substantiated this idea by model calculations for a point charge within a narrow tube, in which the latter was treated either as a perfect conductor or as a Thomas-Fermi metal [6]. The image charges on the tube of the wall produced the expected reduction of the Coulomb potential along the axis of the tube. Our own group has investigated ions in narrow nanotubes at the atomic level, and performed density functional theory (DFT) calculations for a series of alkali and halide ions in carbon and gold nanotubes [7,8]. We confirmed the screening mechanism proposed by Kondrat and Kornyshev and added important details. For small tubes with diameters less than about 0.9 nm, the stable position of the ions is in the center of the tube. The image charge does not reside on the atoms in the wall of the tubes, but is concentrated closer to the ion at the center. We described this effect quantitatively by an effective image radius, which is smaller than the geometrical radius of the tube, making the screening more effective. Also, the strengths of the screening depends on the nature of the wall: Metal tubes screen the ionic charge more effectively than carbon nanotubes. The latter findings are in line with the work of Skinner et al. [9], but their semiclassical calculations also underestimate the screening effect.

Because of their wide potential window and their high ionic concentrations ionic liquids are particularly suitable electrolytes for supercapacitors [10]. Despite their complicated molecular structures the absence of a solvent makes it possible to develop relatively simple models, which greatly help in understanding basic effects. Thus, concepts like overscreening and crowding have been based on continuum models [11,12]. In the same spirit, Lee et. al. [13] and Kornyshev [14] have recently constructed a model for an ionic liquid confined in a narrow pore, where the ions are aligned along the center. With some simplifying assumptions they mapped the statistical mechanics of this ensemble onto the Ising model; in a two-state version positive and negative ions correspond to up and down spin orientations [14], in a three-state version spin zero corresponds to an empty site [13]. This model allows an analytical solution; in the basic form of the two-state model the capacity shows a minimum at zero charge, and symmetrical maxima on each side [14]. In this work, we want to consider another simple model for ion storage in nanotubes, which is based on the observation, that often the cations and anions of ionic liquids have very different sizes [15]. Indeed, in several ionic liquids one kind is an atomic ion like a halide ion. If such a liquid is in contact with a thin

---

[1] ISE member.

nanopore, only the small ions can enter. Therefore, the situation is highly asymmetric, and the tube can attain only one kind of charge. This is a realistic scenario, whose statistical mechanics are rather simple; we explore this case in the following.

2. A model for a chain of ions in a nanotube

We consider a nanotube of length L, which contains N identical monovalent ions aligned along the central axis; a schematic picture is shown in Fig. 1. The charge of the ions is balanced by a counter charge on the wall of the tube. The ions repel each other by a screened Coulomb interaction, which we have previously obtained from DFT calculations [7,8]. We denote by $U(x)$ the screened potential generated by one particular ion along the axis, x being the distance from the ion. At equilibrium and zero temperature the ions are equidistant, with a separation $d = L/N$. Since the potential $U(x)$ decays rapidly, it is sufficient to consider interactions between nearest neighbors only. Therefore, at the minimum energy each ion has the same energy $\epsilon(N) = U(d)$, and for a given number N the energy of the ensemble is $N\epsilon(N)$. Figure 2 shows the potential $U(x)$ for two different tubes: a (10,0) CNT (carbon nanotube) and an (8,8) Au NT (nanotube).

In order to understand things better, we shall build up the model step by step, and consider oscillations of the ions later. In this case the partition function is:
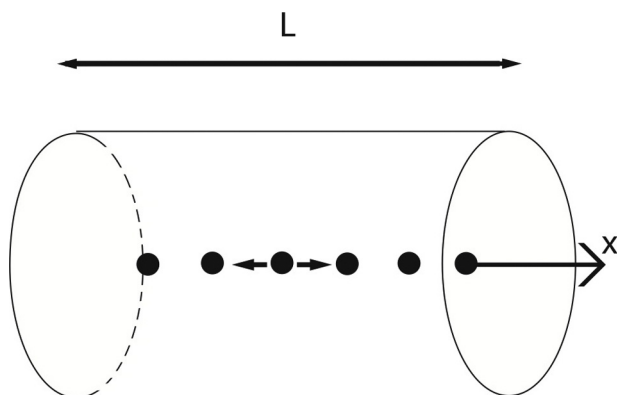
$$Z = \frac{1}{N!} \exp(-\beta\epsilon(N)) \tag{1}$$

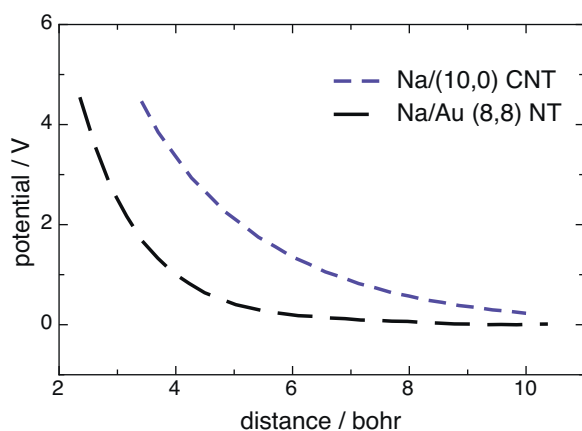**Fig. 1.** Schematic picture of ions in a narrow pore.

Fig. 2. Screened Coulomb potential along the axis of a (10,0) CNT and a (8,8) Au NT. The calculations have been performed for a Na$^+$ ion on the axis, but outside of the ionic radius the potential is independent of the nature of the ion [7,8].

with $\beta = 1/kT$, where k is the Boltzmann constant and T the temperature. The factor $1/N!$ accounts for correct Boltzmann counting and entropy. From this we obtain the Helmholtz free energy as:

$$F = -kT \ln Z = N\epsilon(N) + kT \ln N! \tag{2}$$

In this section we consider the case of large tubes and large N, i.e. the thermodynamic limit. In this case we can use Stirling's formula and obtain:

$$F = N\epsilon(N) + kT[N \ln N - N] \tag{3}$$

It is easy to verify, that the first term is the internal energy $U = N\epsilon(N)$, so the second term is $-TS = kT[N \ln N - N]$, where S is the entropy.

Before we proceed, it is instructive to consider the case of constant energy ϵ. In this case we obtain for the electrochemical potential:

$$\tilde{\mu} = \frac{dF}{dN} = \epsilon + kT \ln N \qquad \epsilon = \text{const.} \tag{4}$$

This is familiar from the theory of an ideal gas at constant volume, or of an ideal solution. Without loss of generality we suppose that the ions are cations. The ions in the tube are in equilibrium with the bulk electrolyte; hence they have the same electrochemical potential $\tilde{\mu}$. The stored charge is Ne_0, where e_0 is the elementary charge. The change $\delta\phi$ in the electrode potential induces a corresponding change $e_0\delta\phi$ in the electrochemical potential. Therefore, the differential capacity C per unit area of the nanotube can be calculated from:

$$\frac{1}{C} = \frac{A}{e_0^2} \frac{\partial\tilde{\mu}}{\partial N} \tag{5}$$

where A is the area of the nanotube. For the case of a constant energy ϵ we obtain:

$$\frac{1}{C} = \frac{A}{e_0^2} \frac{kT}{N} = \frac{kT}{e_0 q} \qquad \epsilon = \text{const.} \tag{6}$$

where q is the charge per unit area. We note that both eq. (4) and eq. (6) diverge as $N \to 0$. At a first glance, taking this limit seems contradictory, since by using Stirling's formula we have supposed that N is large – the case of a short tube will be treated in the next section. We can avoid this difficulty by considering the capacity per unit length and write:

$$\frac{L}{C} = \frac{1}{e_0^2} kT \frac{L}{N} \qquad \epsilon = \text{const.} \tag{7}$$

So the inverse capacity per length diverges as the number of ions per length, N/L, tends to zero. This sort of argument is usually implied when one takes the thermodynamic limit. Exactly the same situation occurs in the thermodynamic derivation of the Langmuir isotherm, which has a divergence for zero coverage, as the number of adsorbed species tends to zero. Indeed, our problem can be considered as the adsorption of a charged species in a nanotube

We now consider the interactions between the particles, and thereby the explicit dependence of $\epsilon(N)$. We note that the entropic term, which gives rise to the divergence, remains the same. So we now obtain for the electrochemical potential:

$$\tilde{\mu} = \frac{dF}{dN} = \epsilon(N) + N\frac{d\epsilon(N)}{dN} + kT \ln N \tag{8}$$

Equation (5) for the inverse capacity remains valid, while eqs. (6) and (7) give the contribution of the entropic part. The inverse capacitance now contains the first and second derivatives of ϵ with respect to N.

We want to introduce the oscillations of the ion into our model; before doing so, we consider the effect that a single classical vibrational mode of frequency ω has on the capacity. Let us consider