

# Development of Thermodynamic Methods for the study of Nanopores

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## 1 ABSTRACT

A statistical mechanical formalism is presented for the calculation of the thermodynamic properties of the water in nanopores of polymer electrolytes, with particular emphasis on the polarization. We describe a method that exploits the variational properties of the Ornstein-Zernicke integral equation.

## 2 INTRODUCTION

The main thrust of the work to be presented in this paper will be the development of statistical thermodynamic methods for application to polymer electrolyte membranes commonly used in a variety of fuel cells [1]. In these devices the anode and cathode are separated by a polymer membrane, which conducts the ionic current (as protons) while the usable electronic current passes through the external circuit. The efficiency of the cell operation, clearly, must be a function of the ionic conductivity of the membrane and thus of the morphology of the latter. A considerable body of structural information about these membranes is now available and it is known that the transport of protons occurs through a network of hydrated channels or pores supported by a hydrophobic matrix or medium that provides the requisite mechanical strength and chemical and thermal stability of the material. The system of pores may be modeled as a network of channels each of which due to their size are referred to as nanopores. The structures of these hydrated nanopores are quite complex and vary from one polymeric material to another, however, for the present study the most relevant feature is the presence of negatively charged anionic groups attached to the pore walls. These groups are either distributed along the interior of the pore walls or may be present at the termini of short chains protruding into the pore interior. Since in the majority of cases the ionic species being conducted are hydronium ions it is evident that these negatively charged groups, which are most often  $\text{SO}_3^-$  groups, will play a critical role in determining the proton diffusion [2].

The state of water within the nanopores is, in general, different from that of bulk water. Neutron scattering

experiments carried out by Lee et al [3] on water confined in nanopores of perfluorinated ionomer membranes shows that the radial distribution functions agree with that of bulk water for only the fully hydrated pores. The precise form that the water adopts under the influence of both pore confinement and the electrical field due to the anionic groups is still not understood [4]. From the above discussion, it is evident that the thermodynamic properties of water in these nanopores will differ from that of bulk water. In this paper we present the framework for calculating the Helmholtz free energy for water in the pore and apply this method for the computation of the polarization of the water. The latter is a very important electrical property that plays significant role in the transport of the protons.

## 3 THE HELMHOLTZ FREE ENERGY

In order to compute the Helmholtz free energy, for which we assume that a classical mechanical formalism to be adequate, a suitable Hamiltonian must be first adopted. In general such a Hamiltonian,  $H$ , will be composed of both particle kinetic and potential energies, the former, however, cancel out and will therefore not be displayed. The remaining terms must appropriately account for all the interactions and energy sources in the system. Each nanopore for simplicity is assumed to be cylindrical in shape with radius  $R$  and length  $L$  in which the fixed sites are modeled as a sequence of negatively charged rings, attached to the pore wall and constituting a lattice. An analytic expression for the field due to such a charge arrangement is available in literature and will not be reproduced here (see [5]). Unlike most traditional fluid systems, in which only an external field is present, in this case the energy of the field due to the anionic sites is a part of the system and must be included:

$$\text{---} \tag{1}$$

The meaning of the various quantities appearing in (1) is as follows:

- (1)  $N$  is the number of water molecules in the pore.
- (2) The center of mass of each water molecule,  $\mathbf{r}_i$ , is located by a vector  $\mathbf{r}_i$  drawn from the origin of a space fixed coordinate frame. The orientation of the dipole  $\mathbf{p}_i$  on the molecule is indicated by polar spherical angles  $\theta_i, \phi_i$ . The symbol  $\mathbf{e}_i$  is the unit vector in the direction of  $\mathbf{p}_i$ .
- (3)  $\mathbf{E}_i$  is the field due to the  $q$  groups at the location of water molecule  $i$ .
- (4)  $\mathbf{E}$  is an external field that probes the properties of the system.
- (5)  $\phi_{ij}$  is the two-body interaction potential between the water molecules. For the purposes of this paper we restrict the analysis to two contributions:-

(a) A hard-core interaction  $\phi_{ij}^{\text{hc}}$ :

$$\phi_{ij}^{\text{hc}} = \begin{cases} \infty & \text{if } |\mathbf{r}_i - \mathbf{r}_j| < r_{\text{hc}} \\ 0 & \text{otherwise} \end{cases}$$

(b) A dipolar interaction  $\phi_{ij}^{\text{dip}}$ :

$$\phi_{ij}^{\text{dip}} = \frac{1}{4\pi\epsilon_0} \left[ \frac{\mathbf{p}_i \cdot \mathbf{p}_j}{|\mathbf{r}_i - \mathbf{r}_j|^3} - \frac{3(\mathbf{p}_i \cdot (\mathbf{r}_i - \mathbf{r}_j)(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{p}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^5} \right]$$

Here,  $r_{\text{hc}}$  is the radius of the hard core and  $\mathbf{1}$  is the unit tensor.

(6) The  $\sum_i$  summation term in the first term of eq. (1) is the energy of the anionic field at the location of the water molecule. In order to compute this energy we consider the relevant water molecule to reside in a cavity of volume  $V$ .

(7)  $\epsilon_0$  is the vacuum permittivity.

(8)

The configuration integral,  $Z$ , the  $N$ -body distribution function,  $\rho_N$ , and the corresponding Helmholtz free energy,  $A$ , can be obtained from the Hamiltonian:

$$(2)$$

$$\rho_N = \frac{1}{Z} \int \prod_i d\mathbf{r}_i d\Omega_i \exp(-\beta H) \quad (3)$$

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The integrations are carried out over the pore volume and orientations of the water dipoles. Once the Helmholtz free energy has been calculated all the thermodynamic properties can be computed from it. We will, however, concentrate our efforts on computing the polarization since that is the source of the permittivity.

#### 4 POLARIZATION CALCULATION

The polarization,  $P$ , is given by the functional derivative of the Helmholtz free energy:

$$P = \frac{\delta A}{\delta E} \quad (6)$$

A functional Taylor expansion and retention of terms up to the first order in the external field gives:

$$P = \frac{\delta A}{\delta E} \quad (7)$$

The function  $\rho_{ij}$  is the two-body correlation function, which is related to the two-body distribution function  $\rho_{ij}$ :

$$\rho_{ij} = \frac{1}{Z} \int \prod_i d\mathbf{r}_i d\Omega_i \exp(-\beta H) \quad (8)$$

In fact it is easy to see that all the distribution functions that appear in the expansion of the polarization given above can be computed once the correlation function  $\rho_{ij}$  is known. Indeed from the two-body distribution function given by eq. (8) the one-body distribution function can be computed by integration:

$$\rho_i = \int d\mathbf{r}_j d\Omega_j \rho_{ij}$$

In the present case where we are interested in calculating the pair correlation function within a nanopore

the problem is rendered more difficult than the more traditional bulk or macroscopic calculation because of the following reasons:-

(1) While the value of  $\rho$  is large it is not large enough for its value to be taken to be infinity. The volume of the nanopore cannot be set equal to infinity and so the thermodynamic limit, often used, cannot be any longer invoked. This limit allows several simplifications that are no longer possible to make.

(2) The topological reduction theorems that can be proved and used in the graphical cluster theory for infinite number of particles become doubtful for this relatively smaller system.

(3) Because of the presence of the field generated by the anionic sites the property of translational invariance is no longer tenable and the resulting simplifications cannot be employed.

Despite the lack of these simplifying features, that can normally be exploited, the Ornstein-Zernicke (OZ) integral can be exactly derived:

$$\hat{h}(r) = \frac{1}{\rho} \left[ \hat{c}(r) + \int \rho \hat{h}(r_1) \hat{c}(r_2) dr_1 dr_2 \right] \quad (9)$$

$$\hat{c}(r) = \hat{h}(r) - \int \rho \hat{h}(r_1) \hat{c}(r_2) dr_1 dr_2 \quad (10)$$

Eqs.(9) and (10) are each others inverse hence by taking their product the Ornstein-Zernicke equation follows immediately:

$$\hat{h}(r) \hat{c}(r) = \hat{c}(r) \hat{h}(r) \quad (11)$$

The function  $\hat{c}(r)$  defined above is the *direct correlation function*. While the OZ equation does provide us with an integral equation for calculating  $\hat{h}(r)$ , the direct correlation function is also an unknown quantity but standard closure methods are available [6] that allow a form to be selected. We will, however, not discuss these details in this brief communication, but present them in a larger future paper [7].

In order to calculate  $\hat{h}(r)$  the OZ equation must be solved. This is done by iterative methods [6], starting with a guessed form in the right hand side, the equation solved numerically to obtain an improved version, which then becomes the input for the next step. The trial

functions generally contain parameters whose values are improved by the calculation. Such an approach is generally used along with the translational invariance and involves intensive computer application. In our case, the problem is even more severe due to the reasons mentioned above. We find, however, that the Ornstein-Zernicke equation can be recast into the form of a functional that possesses variational properties with respect to the trial functions.

## 5 VARIATIONAL PROPERTIES OF OZ

For the purposes of the present discussion it is convenient to write eq.(11) in the form of a matrix functional equation:

$$\hat{h} = \frac{1}{\rho} \left[ \hat{c} + \int \rho \hat{h} \hat{c} \right] \quad (12)$$

Here, a dot means a multiplication by the one body distribution function followed by integration over the continuous variable  $r$ . If we Taylor expand this exact functional equation about a trial function,  $\hat{h}_t$  (such as the one used in a numerical calculation) and retain up to first order terms only:

$$\hat{h} = \hat{h}_t + \int \rho \hat{h}_t \hat{c} \quad (13)$$

It is easy to see that:

$$\hat{h} = \hat{h}_t + \int \rho \hat{h}_t \hat{c} \quad (14)$$

Unfortunately the inverse  $\hat{c}^{-1} / \rho$  contains the unknown function so it is replaced by a second trial function  $\hat{c}_t$ , which could be the same as  $\hat{h}_t$ :

$$\hat{c} = \hat{c}_t \quad (15)$$

Eq. (15) is an approximate solution of the OZ equation in terms of the trial functions  $\psi_1$  and  $\psi_2$ . It can also be shown that this solution obeys:

$$\frac{\delta \langle \psi | \hat{H} | \psi \rangle}{\delta \psi} = 0$$

and is therefore a variational solution of the OZ equation. From a practical point of view the trial functions are taken to depend upon sets of parameters:  $\alpha$  and  $\beta$ , substituted in eq. (15) the resulting equation for  $\psi$  differentiated with respect to each of these parameters and the results set equal to zero. This leads to a set of algebraic equations from which the parameters can be computed. The variational approach will result in a significant reduction in the amount of computing time.

#### 4 HIGH ANIONIC FIELD LIMIT OF POLARIZATION

In the limit of a high anionic field:  $\beta \rightarrow \infty$  and  $\alpha \rightarrow 0$  only the first term of eq.

(7) makes a significant contribution to the polarization, furthermore, the one-body distribution function assumes a very simple form

$$\psi_1 = \frac{1}{\sqrt{\pi}} e^{-\beta^2 r^2} \quad (16)$$

With:

$$\psi_2 = \frac{1}{\sqrt{\pi}} e^{-\beta^2 r^2} \cos(\theta) \quad (17)$$

The integration over the angular variable  $\theta$  can be immediately carried out to yield an expression for the polarization:

$$P = \frac{1}{\sqrt{\pi}} \int_0^\infty r^2 e^{-\beta^2 r^2} dr \quad (18)$$

This is a new result and contains a Gaussian factor that arises from the field energy. It is this factor that leads to the phenomenon of dielectric saturation. In other more traditional derivations [5] dielectric saturation can only be observed if it is assumed that the anionic field is either a constant or a very slowly varying function of  $r$ , neither of which conditions hold in these nanopores.

#### REFERENCES

[1] T. A. Zawodzinski Jr., C. Derouin, S. Radzinski, R. J. Sherman and S. Gottesfeld, *J. Electrochem. Soc.* **140**, 1041 (1993).  
 [2] S. J. Paddison, R. Paul and T. A. Zawodzinski Jr., *J. Chem. Phys.* **115**, 7753 (2001).  
 [3] E. M. Lee, R. K. Burgess, D. J. Barnes, A. K. Soper, and A. R. Rennie, *Macromolecules* **25**, 3106 (1992).  
 [4] M. Laporta, M. Pegorara, and L. Zanderighi, *Phys. Chem. Chem. Phys.* **1**, 4619 (1999).  
 [5] R. Paul and S. J. Paddison, *J. Chem. Phys.* **115**, 7762 (2001).  
 [6] J. P. Hansen and I. R. McDonald, "Theory of Simple Liquids", Academic Press, 109-133, 1976.  
 [7] R. Paul and S. J. Paddison, *J. Chem. Phys.*, submitted.