The Modeling of the Polarization of water in the Nanopores of Polymer Electrolyte Membranes

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Abstract

Protons are ubiquitous mediators of energy transformation in many systems (1). In the context of electrochemical systems, polymer electrolyte membrane (PEM) fuel cells are considered promising autonomic energy converters, exhibiting: high efficiencies, low pollution levels and technological versatility (2). This promising prospect promotes an intense interest in PEMs. While the presence of liquid-like water in the nanoporous structure of current PEMs promotes high rates of proton transfer, it imposes penalties associated with low operating temperatures and proper water management in the fuel cell (3). In view of the present restrictions, obtaining high proton conductivities with small amounts of water, tightly bound to a stable host polymer and, thus, restricted in mobility, could result in major technological breakthroughs (4,5). Clearly, this requires fundamental understanding of both the mechanisms of proton transfer and the nature and character of the water in these materials. The present theoretical investigation addresses the latter issue, and extends the theoretical work previously developed by the authors (6,7).

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 (8) 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. From the above discussion, it is evident that the thermodynamic properties of water in these nanopores will differ from that of bulk water. The problem is rendered more difficult than the more traditional bulk or macroscopic calculation because of the following reasons:-

(1) While the value of N, the number of water molecules, 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:

$$h(1,2) = c(1,2) + \int d3c(1,3)\, n_1(3)\, h(3,2)$$

Here, h is the *pair correlation function*, c is the *direct correlation function*, and n_1 is the *one-body distribution function*. The arguments of the functions and the integration variables are shorthand representations of the center-of-mass and orientation of each water molecule. Once h has been computed the relevant thermodynamic properties can be calculated by using standard formulae from statistical thermodynamics.

In order to calculate h the OZ equation must be solved. This is done by iterative methods (9), 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. Using a matrix notation to represent the OZ equation:

$$\mathbf{h} = \mathbf{c} + \mathbf{c}.\mathbf{h} = \mathbf{c} + \mathbf{h}\cdot\mathbf{c} \text{ or } \mathbf{F}(\mathbf{h}) \equiv \mathbf{h} - \mathbf{c} - \mathbf{h}\cdot\mathbf{c} = \mathbf{0}$$

We find that a variational solution, $\mathbf{h}_v$, for the integral equation may be written as:

$$\mathbf{h}_v = \mathbf{h}_\mathbf{t} - (\mathbf{1} + \mathbf{h}_\tau)\cdot\mathbf{F}(\mathbf{h}_\mathbf{t})$$

Here, $\mathbf{h}_t$ and $\mathbf{h}_\tau$ are trial or guessed functions depending upon sets of initially chosen parameters with respect to which $\mathbf{h}_v$ displays stationary properties.

In this work we consider the well-known direct correlation function derived for hard spheres (9):

$$c(x) = -\lambda_1 - 6\eta\lambda_2 x - \frac{1}{2}\eta\lambda_1 x^3$$

Here, x is related to the distance between the two hard spheres and the other parameters will be employed as variational parameters in order to adapt this function to the interior of a charged nanopore.

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