



Simulation of osmotic pressure across an amorphous semipermeable membrane

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ABSTRACT

Molecular simulations were employed to investigate osmosis for systems far from ideal conditions. Osmotic pressure was calculated for of a fluid mixture separated from a pure fluid by a fictitious semipermeable membrane using Gibbs ensemble Monte Carlo (GEMC) and compared with that of the two phases separated by a physical amorphous polyamide membrane using molecular dynamics. The calculated osmotic pressure for these two simulation set-ups was compared with various predictive models for a range of solute concentrations and solution densities. Both equilibrium-based theories, which are mostly limited in their applicability to near-ideal conditions or low solute concentrations, and non-equilibrium theories that extend to more concentrated solution conditions fared well against the GEMC simulation in their expected range, but did not adequately predict the osmotic pressure calculated according to simulations across the physical membrane for finite system size and under the limiting conditions considered. The discrepancies were particularly large for high solute concentrations and low solution densities. The observed differences are discussed in terms of solution inhomogeneities resulting from particle-membrane interactions.

1. Introduction

Osmotic pressure (Π) across a semipermeable membrane results from selective permeation of the solvent (water) towards the solute-rich phase. While Π is generally considered to be a function of solution conditions and permeability of the membrane, recent studies suggest that the presence of the membrane as a physical body that exerts forces on the environment and reacts to it (deforms) may influence the measured osmotic pressure, where the surface area to volume ratio is comparable. Much attention has been given to predictive and semi-empirical models that consider solution thermodynamics, but only recently the role of a physical membrane has been critically analyzed.

Computer simulations provide a direct method for evaluating Π by explicitly including a selective barrier to diffusion of one of the components within the simulation box [1,2]. Simulations allow exact control of the size, structure, flexibility, and interaction of the membrane, making it possible to isolate the contribution of each to the osmotic pressure. Early computational efforts to study membrane permeability and the osmotic effect represented membranes as either ordered arrays of particles, or as a porous medium with well-defined and ordered pores. Pioneering works by Murad and coworkers showed the validity of van't Hoff's relationship for the osmotic pressure [3] using simple representation of semipermeable membranes modeled as an ordered fcc

lattice of a single or few molecular layers [4,5]. One of their principal findings was the deviation from van't Hoff's relation at low solute fractions for nonideal mixtures where solute particles differ from the solvent by size or interaction strength [6].

Research based on density functional theory (DFT) focused on the structure of the fluid in the vicinity of the membrane. Bryk et al. [7] developed DFT model for the phase behavior of a Lennard-Jones (LJ) fluid in contact with a permeable wall of finite thickness using DFT and showed how the permeability of the wall modifies the surface phase behavior of the fluid when compared with an impermeable surface. These authors later extended their model to study the structure and thermodynamic properties of a polydisperse fluids (i.e., a mixture with an infinite number of components) near the membrane [8]. Yang et al. [9] tested DFT predictions for homogeneous solution using extensive grand canonical Monte Carlo simulations, and found that the dispersion term in the DFT functional must be corrected for better prediction in the case of mixtures. Furthermore, the authors confirmed van't Hoff's law at low densities, revealing nearly identical behavior for different diameter ratios of the solute and solvent. However, they found that the van't Hoff prediction underestimates the osmotic pressure beyond solute volume fraction of ~ 0.4 , where the interaction between particles begins to play a role, similar to finding in previous studies by Murad et al. [6].

Pitzer and coworkers provided a thermodynamically rigorous

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development for the expression of the osmotic pressure, based on the dissolution of ions in water at high ionic strengths [10–12]. The authors introduced a variable second virial coefficient in their treatment of the osmotic pressure of concentrated electrolyte solutions of monovalent and divalent ions. Pitzer's model was shown to accurately predict the osmotic pressure of 2–1 and 2–2 concentrated electrolyte solutions [13], while simpler models that neglect solute-solvent interactions show large deviations for molalities greater than 1.0. It should be noted, however, that determination of the Pitzer coefficients is experimentally difficult and hence reduces the utility of the model. Recently, solute chemistry was also shown to play a determining role in its effect on the osmotic pressure as it defines the effective solute size due to bound waters, in addition to the solute-membrane interactions [14]. This effect was notable for charged as well as polar solutes. Further studies using simplified models predicted that membranes with stronger attractive interactions with the solvent molecules have significantly larger solvent permeation rates that increase significantly with increase in temperature [15]. Depending on their chemical nature, it was shown that ions may not penetrate even neutral membranes due to large ion-water clusters that have high energies of desolvation, whose large effective size prevents them from permeating the membrane [16–19].

Nanofiltration and reverse osmosis membranes used for separation of small molecules or ions have quite a complex functionality and structure that affect their performance. The rejection layer of most commercially available nanofiltration and reverse osmosis membranes is an ultra-thin film formed in situ at the interface of two immiscible solvents, resulting in a dense layer at the reaction zone whose properties essentially determine the performance (flux and rejection) of the membranes [20]. Molecular models reveal the highly heterogeneous void structure of polyamide membranes [21–24], which is argued to be the primary factor that affects water dynamics within the membrane [25]. Recent molecular dynamics (MD) studies suggest that real membranes that are an order of magnitude thicker than the simulated ones do not have low energy pathways for ion transport and exhibit resistance to ionic diffusion due to charge separation [26], while nonequilibrium MD simulations reveal that film deformation due to flow under pressure gradient affects film void structure and thereby the local structure and permeability of water and ions [27]. Clearly, accumulation of solute and solvent near and within the membrane affects its rejection, and hence influences the measured osmotic effect.

In this work, we focus on the effect of solution inhomogeneous and nonideality on osmosis. Apart from being of theoretical interest, applications of such limiting conditions include osmotic dehydration of fruits and vegetables [28] or the extraction of essential oils [29]. We compare the osmotic pressure calculated across a fictitious non-interacting semipermeable barrier and across an amorphous polyamide membrane of finite thickness. Finite systems where the surface area to volume ratio is comparable have received increasing attention for various applications in microfluidics [47,48] and include sample concentration in analytical chemistry, water-powered actuator based on osmosis [49], and biologically-relevant phenomena or biotechnological applications such as osmotically driven flow in microchannels [50], drug delivery [51], and osmotic pumps to induce concentration gradients [52]. We analyze the range of applicability of the van't Hoff equation, of simple thermodynamic models for non-ideal solutions, and of the mechanical model of Granik et al. [30] for the two membrane configurations. The Granik model was chosen for comparison as it was recently shown to fare well with experimental results for sucrose [31], though with a tendency to overpredict the osmotic pressure at higher solute densities.

2. Methods

2.1. Theoretical models of osmotic pressure

The van't Hoff equation is commonly used for approximating the osmotic pressure Π for dilute solutions,

$$\Pi = RTc_2 \quad (1)$$

where R is the universal gas constant, T is the temperature, and c_2 is the concentration of the solute. The simple form of the van't Hoff equation arises from the assumption of solution ideality, such that the osmotic effect is accounted for only by the entropy of mixing. In other words, chemical interactions within the system are neglected.

The Gibbs-Duhem equation relates the solvent activity to the solute activity and allows for a more rigorous evaluation of the osmotic pressure by accounting for the non-ideal solute-solvent interactions. Accordingly, the osmotic pressure of two systems separated by a semipermeable membrane and in thermal equilibrium is related to the solvent activity coefficient by

$$\int_{P_0}^{P_0+\Pi} \frac{\bar{v}(P)}{RT} dP = -\ln(x_1\gamma) \quad (2)$$

where P_0 is pressure of pure solvent compartment, \bar{v} is the partial volume, x_1 is the mole fraction of the solvent in the mixture, and γ is the activity coefficient at the temperature and pressure of the mixture. For incompressible solutions, the partial molar volume can be assumed constant for a given temperature. If the dependence of the partial volume on pressure is neglected, simple integration of Eq. (2) results in an explicit formula for osmotic pressure,

$$\Pi = -\frac{RT}{\bar{v}} \ln(x_1\gamma). \quad (3)$$

The activity coefficient in Eqs. (2) and (3) contains all contributions to non-ideality of the solution, such as molecular size, specific and nonspecific interactions. This approach was recently studied as a means of calculating activity coefficient directly from osmotic pressure measurements [2].

Ferrari and coworkers [30] derived an expression for the osmotic pressure for incompressible fluids based on the flux of diffusing species. Their expression in the case of pure solvent and a binary solution separated by a semipermeable membrane is given by

$$\Pi = \frac{RTm_2V}{1+(1+V)m_2/m_1} \quad (4)$$

where m_1 and m_2 are the volume molal concentrations of the solvent and solute, respectively, and V is the solution volume. All of the above expressions (Eqs. (1)–(4)) are derived from fundamental relations and hence they necessarily impose limitations beyond their explicit assumptions, particularly ones involving membrane structure and interactions. These models are therefore limited in their validity towards conditions of practical system. To broaden their range of applicability, empirical adjustable parameters and correlations are often used for practical applications for a given system of interest.

2.2. Computational methods

2.2.1. Force field

The molecular models considered involve interaction between neutral spherical particles (solvent, solute, and membrane) modeled by the shifted Lennard-Jones (LJ) potential,

$$U_{LJ} = 4\epsilon_{ij} \sum_{i<j \subset D} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] - U_{LJ,cut}, \quad r_{ij} \leq r_{cut} \\ U_{LJ} = 0, \quad r_{ij} > r_{cut} \quad (5)$$

where

$$U_{LJ,cut} = \left[\left(\frac{\sigma}{r_{cut}} \right)^{12} - \left(\frac{\sigma}{r_{cut}} \right)^6 \right] \quad (6)$$

r_{ij} is the distance of two interacting particles i and j . σ_{ij} and ϵ_{ij} are the Lennard-Jones interaction parameters corresponding to effective particle diameter (units of distance) and interaction potential (units of energy), respectively. All calculated quantities are given in reduced LJ

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