

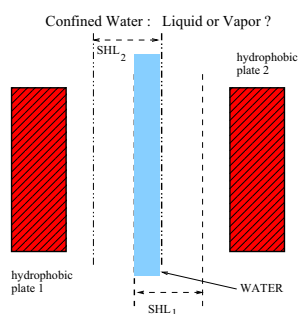
Temperature dependence of the evaporation lengthscale for water confined between two hydrophobic plates



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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 October 2014

Accepted 20 January 2015

Available online 7 February 2015

Keywords:

Water hydrogen bonding
Confined liquid water
Hydrophobic plates
Density functional theory
Density profiles
Evaporation lengthscale
Temperature effect
Hydrophobic hydration
Hydrophobic interactions

ABSTRACT

Liquid water in a hydrophobic confinement is the object of high interest in physicochemical sciences. Confined between two macroscopic hydrophobic surfaces, liquid water transforms into vapor if the distance between surfaces is smaller than a critical separation, referred to as the evaporation lengthscale. To investigate the temperature dependence of the evaporation lengthscale of water confined between two hydrophobic parallel plates, we use the combination of the density functional theory (DFT) with the probabilistic hydrogen bond (PHB) model for water–water hydrogen bonding. The PHB model provides an analytic expression for the average number of hydrogen bonds per water molecule as a function of its distance to a hydrophobic surface and its curvature. Knowing this expression, one can implement the effect of hydrogen bonding between water molecules on their interaction with the hydrophobe into DFT, which is then employed to determine the distribution of water molecules between two macroscopic hydrophobic plates at various interplate distances and various temperatures. For water confined between hydrophobic plates, our results suggest the evaporation lengthscale to be of the order of several nanometers and a linearly increasing function of temperature from $T = 293$ K to $T = 333$ K, qualitatively consistent with previous results.

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1. Introduction

Liquid water in a hydrophobic confinement has long been the object of high scientific interest in physics, chemistry, and biology

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[1–8]. Such systems (either nano- or micro-scale) play an important role in many natural phenomena and technological processes, such as those in zeolites and clays [9], carbon nanotubes and nanofluidics [10–12], ion channels [13], living cells interior [14], water transport in plants [15], etc. Confined fluids (water being most interesting among them) exhibit quite unusual properties that are not observed in the bulk [16–24]. On the other hand, the peculiar properties of water near hydrophobic surfaces give rise

to such amazing phenomena as hydrophobic hydration and hydrophobic interaction [25–32]. These are believed to constitute an important (if not crucial) element of a wide variety of physical, chemical, and biological phenomena [33–39], such as self-assembly of amphiphiles into micelles and membranes [40], gating of ion channels [41], etc. Hydrophobic interactions are also important in many technological and industrially significant processes (such as wetting, froth flotation, adhesion, etc.) [42].

Hydrophobic hydration is the thermodynamically unfavorable dissolution of a hydrophobic particle (microscopic or macroscopic), whereof the accommodation in water is accompanied by an increase in the associated free energy due to structural (and possibly energetic) changes in water around the hydrophobe. Since the total volume of water affected by two hydrophobes is smaller when they are close together than when they far away from each other, there appears an effective, solvent-mediated attraction between them which is referred to as hydrophobic attraction. Most properties of hydrophobic interactions may be unambiguously determined from the analogous properties of hydrophobic hydration; the former can be regarded as a partial reversal of the latter.

Understanding these phenomena remains limited and the development of predictive models that are capable of estimating their dependence on temperature, pressure, and other thermodynamic variables of the system is important. Further progress in this direction requires more experimental and theoretical studies clarifying how such forces depend on external parameters, hydrophobe size and shape, and their surface properties.

The simplest model of solvent-mediated interaction between large hydrophobes can be represented by liquid water confined between two infinitely parallel hydrophobic plates. This model has been the object of numerous theoretical and simulational studies [1–8]. It was observed that, even under conditions where the bulk liquid is stable, if the separation between two plates is sufficiently small, the liquid confined between the plates evaporates therefrom so that the system transforms into “vapor confined between two hydrophobic plates”. The crossover separation, below which the liquid between two hydrophobic plates becomes metastable (despite being stable in the bulk) and transforms into vapor, is referred to as the evaporation length scale [6].

A similar, although not equivalent phenomenon has been observed in nanofluidics. For example, studying the filling of carbon nanotubes (CNTs, of diameter of about 1 nm) with water, it was found that the nature of water inside a CNT changes dramatically with the CNT diameter; water is stabilized in a vapor-like phase in smaller CNTs (of diameter 0.8–1.0 nm), in an ice-like phase for medium-sized CNTs (of diameter 1.1–1.2 nm), and in a liquid-like liquid phase for larger CNTs (of diameter greater than 1.4 nm) [7].

Although the evaporation lengthscale is an important quantity for the wide variety of aforementioned phenomena and processes involving hydrophobic and confinement effects, its dependence on various thermodynamic parameters has been hardly studied even for simplest systems. Only in Ref. [6] the comparison of water evaporation lengthscale with that of other common liquids was carried out in the framework of the classical thermodynamics by using actual thermophysical property data in a wide range of temperatures.

In this paper, we attempt to shed more light on the temperature dependence of the evaporation lengthscale of water confined between two hydrophobic parallel plates. This can be achieved by examining the distribution of water molecules between the plates at different interplate distances in a range of temperatures of interest.

Along with computer simulations, the formalism of the density functional theory (DFT) [43–46] is widely used for studying the fluid density profiles near rigid surfaces [47,48]. It usually treats the

interaction of fluid molecules with a foreign surface in the mean-field approximation whereby every fluid molecule is considered to be subjected to an external potential, due to its pairwise interactions with the molecules of an impenetrable substrate. This external potential gives rise to a specific contribution to the free energy functional. The minimization of the latter with respect to the number density of fluid molecules (as a function of the spatial coordinate \mathbf{r}) provides their equilibrium spatial distribution.

The application of the DFT formalism to water-like (non-spherical) molecules, whereof the pairwise intermolecular potential depends not only on the distance between molecules but also on their mutual orientations, is practically extremely difficult due to the multifold configurational integrals involved. Furthermore, the effect of a hydrophobic surface on the ability of fluid (water) molecules to form hydrogen bonds had been also ignored in the conventional DFT.

These problems can be now partly alleviated by combining the DFT formalism with the recently developed probabilistic hydrogen bond (PHB) model [49–55] for hydrogen bonding between water molecules in the vicinity of a foreign surface. This model provides an analytic expression for the average number of hydrogen bonds that a water molecule can form as a function of its distance to the surface. Knowing this expression, one can implement the effect of the hydrogen bonding of water molecules on their interaction with the hydrophobic surface into DFT, which is then employed to determine the distribution of water molecules between two macroscopic hydrophobic infinitely large plates at various interplate distances and various temperatures.

2. The combination of the DFT formalism with the PHB model

Before presenting our results for the temperature dependence of the evaporation lengthscale of water confined between two hydrophobic plates, let us outline the combination of the DFT formalism [43–48] and PHB model [49–55] which allows one to find the water density profiles between two plates while *explicitly* taking into account the effect of water–water hydrogen bonding on the hydrophobe–fluid interactions. We will first briefly describe the PHB model then present its implementation into the DFT formalism.

3. The outline of a probabilistic approach to water–water hydrogen bonding near a hydrophobic surface

The PHB model [49,50] considers a water molecule, whereof the location is determined by its center, to have four hydrogen-bonding (hb) arms (each capable of forming a single hydrogen bond) of rigid and symmetric (tetrahedral) configuration with the inter-arm angles $\alpha = 109.47^\circ$. Each hb-arm can adopt a continuum of orientations. For a water molecule to form a hydrogen bond with another molecule, it is necessary that the tip of any of its hb-arms coincide with the second molecule. The length of an hb-arm thus equals the length η of a hydrogen bond.

The hydrogen bond length η is assumed to be independent of whether the molecules are in the bulk or near a hydrophobic surface. The characteristic length $\tilde{\eta}$ of pairwise interactions between water and molecules constituting the substrate (flat and large enough to neglect edge effects, with its location determined by the loci of the centers of its outermost, surface molecules) plays a simple role in the hydrogen bond contribution to hydration or hydrophobic interaction [50–52]. It ($\tilde{\eta}$) only determines the reference point for measuring the distance between water molecule and substrate, so it will be set equal to η .

Consider two infinitely large hydrophobic plates, 1 and 2, immersed in liquid water (Fig. 1). Even if the intrinsic hydrogen

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