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Hydrophobic force, a Casimir-like effect due to hydrogen-bond fluctuations

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HIGHLIGHTS

- Molecular mean field theory consistent with inherent sum rule of water.
- Boundary conditions specific to confining surface type analyzed for molecular fields.
- Free energy deduced using Green's functions envisaged in bulk water description.
- Casimir mechanism manifest in long range hydrophobic force and temperature dependence.
- Interfacial tension deduced from modified solvent dynamics near hydrophobic surfaces.

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ABSTRACT

Hydrophobic force, interfacial tension, and transverse density profile in a confined water system are addressed from first principles of statistical mechanics in a lattice model for water. Using the molecular mean field theory technique we deduce explicit expressions for each of the above mentioned phenomena and show that hydrophobic force is a manifestation of a Casimir-like effect due to hydrogen-bond fluctuations in confined water. It is largely influenced by the long range correlations of orientational fluctuations. Furthermore, the temperature dependence of hydrophobic force between large non-polar surfaces is suggested to be different from that between small solutes. The mechanisms contributing to characteristic behavior in each case are identified. In the case of large surfaces, the prevalence of discrete fluctuation modes in the confinement direction and their entropic contribution to the overall free energy dominate the temperature dependence. Mode discretization is also implicated in the variation of interfacial tension with separation distance between confining surfaces and characteristic density profile of the confined fluid. All the computations are parameter free and compare favorably with results of molecular dynamics simulations and experiments.

1. Introduction

The hydrophobic effect is considered the major driving force in a broad range of phenomena such as protein folding, self-assembly of amphiphilic moieties, oil–water demixing, and surface dewetting (e.g. lotus leaf effect). These phenomena occur in aqueous solutions or when apolar surfaces are in contact with water as a consequence of low solubility of non-polar molecules in water and an ensuing attractive force between them, called the "hydrophobic force". Frank and Evans in 1945 postulated from their free energy studies on apolar solutions that water structure at a hydrophobe–water interface gets modified in the direction of greater "crystallinity" and in a bid to reduce the entropy cost due to each such interface, liquid water induces association of hydrophobes [1]. The so-called "iceberg model" was envisaged later by Kauzmann to

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heuristically explain the energy pathway of protein folding [2], where he reasoned that starting from a diffuse chain of amino acids a protein folds until non-polar residues collapse out of hydrophobic force of attraction and eventually bury themselves into a core thereby exposing only polar residues to water. These seminal papers inspired more than a generation of researchers [3–18] to explore the role of water and its inherent fluctuations in giving rise to hydrophobic force between small and large non-polar surfaces (references in reviews [19–22]). Furthermore, direct force measurements carried out by Israelachvili and his coworkers over past three decades show that hydrophobic interaction strength monotonically varies with separation distances up to about 100 Å [22], which is larger than typical lengthscales that exist in simple molecular liquids. It is hence pertinent to ask: (a) Is liquid water characterized inherently by large lengthscale fluctuations unlike simple liquids? (b) How do these fluctuations modify in the presence of hydrophobic surfaces and inflict an attraction between the surfaces? To answer these questions, we developed a mean field framework to handle hydrogen bonding in water [23], analyzed the properties of hydrogen bond fluctuations in bulk water and apply it here to the case of water confined between hydrophobic surfaces.

Various physical mechanisms have been proposed to understand the origin of hydrophobic force, some generic to any fluid such as metastability of confined fluid [24,13], dewetting-induced cavitation under liquid–vapor coexistence conditions [25], fluid structuring effects [26–28] and some, dependent on surface details like correlated dipolar fluctuations [29–31], charged bilayer patches [22], nanobubble centers on surfaces [32,33,17]. The above phenomenological descriptions, however, are either envisaged in a narrow range of fluid conditions or specifically depend on the hydrophobization pattern on surfaces. Hydrogen bonds and their dynamics endow liquid water with distinct thermodynamic properties [34–36]. The (in)ability of a solute to hydrogen-bond with water molecules determines the configurational space of such solutes in aqueous solutions. Our calculational framework envisages hydrogen bond fluctuations in terms of suitable Green's functions generic to associating molecular fluids. Furthermore, the framework can be applied to the case of confined water where the presence of hydrophobic surfaces alters boundary conditions for the same Green's functions and consequently causes net free energy to depend on the separation distance between the surfaces. The framework can also be utilized in the context of physical situations envisaged by previous studies which are cited above.

Liquid water constitutes a network of hydrogen bonds fluctuating at a picosecond timescale. Each water molecule constitutes an oxygen which has four bonding arms, two arms due to positively polarized hydrogen atoms and the other two arms due to negatively polarized lone-pair electrons. Hydrogen bond formation depends on the orientation of the participating water molecules and is specific to the polarity of interacting bond arms. Whenever a hydrogen bond breaks the respective molecules reorient and explore new bonding configurations. As a consequence, over large regions of the liquid the sum of the number of bonded arms and the number of unbonded arms should be equal to four times the number of water molecules. This "sum rule" [23] needs to be accounted for in a statistical description of liquid water in order to elucidate the contribution of orientational fluctuations to the total entropy of the liquid, in addition to the translational entropy associated with density fluctuations in the liquid. Effective-charge interaction models of water such as TIP3P, TIP5P [37–39] provide successful instances of (implicitly) envisaging essential features of hydrogen bonding and associated bond fluctuations consistent with the sum rule. In a large scale molecular dynamics simulations of TIP5P and TIP3P models at ambient conditions we found that density fluctuations are typically short ranged and extend no further than about 12 Å; whereas dipolar orientations of water molecules, which are directly receptive to hydrogen-bond fluctuations, are correlated over large distances, at least up to 75 Å. Two correlation lengths of order 5.2 Å and 24 Å were inferred [40]. The range of Coulomb interactions envisaged in these models, surprisingly, has little effect on the asymptotic behavior of the dipolar orientational correlations [40]. This study revealed the presence of large lengthscales in liquid water, despite the inter-molecular hydrogen bond interaction having only a short range dominance ($\sim$2 Å).

Small hydrophobic surfaces affect the fluctuations of water molecules dominantly for those at the interface. Due to the inability of non-polar molecules to hydrogen-bond with water, the orientational configuration space for interface water molecules is restricted [6,41–43]. We envisaged this aspect of hydrophobe–water interaction in a model study where two mesoscopic non-polar surfaces interact with bulk water. The net change in free energy was deduced in terms of orientational correlations between water molecules at one interface and those at the other. The deduced force between the surfaces is attractive in nature and exponentially decaying with a range of 12 Å which is in striking agreement with surface force apparatus measurements [40]. We ascertained that the temperature dependence of interaction strength is due to competing terms, i.e., orientational correlation function, coupling parameter used to model surface–water interaction and the kT term in the free energy expression, among which the kT term perhaps dominates the temperature dependence of the interaction. For the case of large hydrophobic surfaces, correlations in confined water need to be ascertained. To simulate such a system the surfaces need to be several times larger than the longest correlation length in the system in order to obtain proper equilibrium conditions. This requires a huge system size that would render the simulation prohibitively resource intensive. In addition, the accompanying free energy change could be very small due to the weak nature of correlations at large distances. We hence take an analytic route to describe hydrogen bond fluctuations in water and the effect of spatial confinement on them.

Large hydrophobic surfaces confining water disrupt the hydrogen-bond network fluctuations at the interface, substantially more than mesoscopic non-polar solutes. In addition, the spatially extended surfaces present boundary conditions to the fluctuations in water and restrict the fluctuation modes to a discrete set in the confinement direction. The setting is ideally suited for fluctuation-induced force between the surfaces driven by thermal energy in confined water. Forces of this nature are generically called *Casimir forces*, named after the Dutch mathematician Casimir who first deduced a fluctuation-induced force in the case of electromagnetic field fluctuations confined between conducting plates [44,45]. Such forces are