Final project for course 8.334 5/18/12

Modeling Hydrophobicity as Constraints on Rotational Freedom of Water-like Particles in 2D

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A predictive theory of hydrogen-bonding between water molecules is essential for the understanding of hydrophobicity. In this paper I review well-known models of water and the principles of LCW's theory of the hydrophobic effect. Based on the MB model, I construct a Hamiltonian for the orientation field of flexible hydrogen bonds in two dimensions. I couple a concentration of hydrophobic particles to the field by locally constraining degrees of freedom in the system. The model shows criticality under extreme conditions.

Introduction

Water has received renewed interest from scientists in the last decades as part of the efforts to construct a theory of the hydrophobic effect. Those efforts are in turn motivated by major gaps in areas of biophysics, such as protein folding. Despite many years of research, water is not yet fully understood. In this paper I start by reviewing a couple of statistical models for water which have had large impact on scientific literature. I continue by describing a current theory of the hydrophobic effect. Based on this theory, I suggest which properties of water are the most essential to model in order to better understand the hydrophobic effect. I then describe the MB model for water and the variation of it that I explored. I conclude by incorporating small hydrophobic particles into the model and examining their effect of its critical behavior.

Statistical models of water

Water exhibits anomalous properties that have interested scientists for many decades. The literature contains many statistical models that aim to explain those properties. Some of these models account for the diminution in volume that water exhibits upon melting, the maximum in water density at low temperatures, and the minimum in thermal compressibility. Still, there is only partial agreement between quantitative predictions of theory for thermodynamics of water with experiments and simulations. In addition, theory does not give exact predictions for the behavior of a small number of water molecules near amphiphilic surfaces.

Most of the statistical models assume that the interaction between water molecules is dominated by hydrogen bonding. One of the most well-known models of this kind was presented by Pople in 1951 [1]. Pople assumed that hydrogen bonds between water molecules are arranged in tetrahedral geometry. The bonds are distorted by deviations of the molecules' orientations from that geometry. Based on these assumptions, Pople calculated a radial density distribution for the first three shells around one molecule of water. He argued that the bending of the bonds allows some of the second and third shell molecules to collapse into regions nearer the central molecule, thus causing a large-scale filling up of the region between the first and second shells.

The first lattice model of that kind was published by Bell in 1972 [2]. The model describes a BCC lattice, each site of which can be either empty or occupied by a water molecule. Each molecule forms hydrogen bonds with four out of its eight nearest neighbors. Since the geometry of the bonds must be tetrahedral, there are only two possible choices of neighbors. Therefore, molecules can bind to sites on one or the other tetrahedral sub-lattices of the BCC lattice. Bell included energy gain for hydrogen bonding, as well as energy loss for "close packing", i.e. bonding between molecules from different sub-lattices. Based on these interactions, Bell calculated density curves as function of temperature for different values of pressure. He showed that at low pressures his model exhibits a local density maximum in finite temperatures. In agreement with experiments, Bell's model also showed very weak temperature dependence of the average number of hydrogen bonds per molecule. Until that time this feature has been ascribed to distortion of hydrogen bonds, a property that does not exist in Bell's model.

LCW theory of the hydrophobic effect

Lum, Chandler and Weeks (LCW) pioneered in constructing a quantitative theory of the hydrophobic effect [3,4]. According to LCW, the key interaction in the hydrophobic effect is hydrogen bonding between adjacent water molecules. In theory, pure water can be in states where a) most of the polar sites of the molecules are hydrogen-bonded to each other and b) a lot of freedom is allowed in the motion of the molecules without breaking hydrogen bonds. However, since water molecules cannot hydrogen-bond with hydrophobic particles, mixing the two together changes the picture. The exact effect of the mixing depends on the size of the hydrophobic particles. For a hydrophobic sphere of radius $r{\sim}a$, where a is the characteristic length of a hydrogen bond, water molecules adjacent to the sphere's surface will maintain their hydrogen bonds. However, they will lose translational and rotational entropy due to the excluded volume inside the sphere. In contrast, for $r \gg a$ water molecules near the hydrophobic surface will be forced to break their hydrogen bonds. The resulting attenuated interaction between the water molecules near the surface will lead to large fluctuations in the local water density. These fluctuations can lead to strong attractions between close hydrophobic surfaces.

LCW theory greatly contributes to the understanding of the hydrophobic effect. However, since current models of water do not excel in deriving quantitative predictions from hydrogen bonding interactions, the LCW theory has not yet been fully integrated into a predictive theory for hydrophobic interactions. In order to do that, models of water should be able to describe the trade-off between the energy of hydrogen bonds and the entropic constraints that arise from maintaining those bonds near hydrophobic surfaces. In addition, such models should describe the behavior of small numbers of water molecules that cannot hydrogen-bond near large or low-curvature surfaces.

In this work I approach the first challenge out of those two. I first modify an existing model of water by focusing on rotational degrees of freedom of water-like particles. I then examine critical properties of the system using the language of Statistical Field Theory. Lastly, I probe the effect of entropic constraints on the system.

Model

The water model that I explore here is based on Ben-Naim's water-like particles [5]. These particles are 2D rigid discs with a certain number of hydrogen-bonding arms. The arms are symmetrically distributed around the circumference of each particle (see fig. 1(a)). The special case of particles with three such arms is referred to in more recent papers as the Mercedes-Benz (MB) model [6]. Two such particles form a hydrogen bond between them when two of their arms point toward each other. The maximal energy-gain from bonding is received when the two arms are perfectly aligned. It should be noted that unlike in real water, there is no directionality of the hydrogen bonds; two particles can interact through any pair of arms. Clearly, in the ground state of a system of such particles, the particles are arranged in the sites of a hexagonal (honeycomb) lattice, with all arms aligned along the lines that connect neighboring sites (see fig. 1(b)).

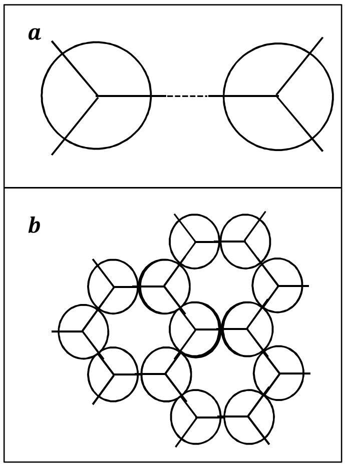

Figure1. Water-like particles of Ben-Naim and the MB model. Each particle has three hydrogen-bonding arms. a) the lowest energy of a bond is when two arms are aligned. b) in the ground state the particles are arranged as a hexagonal lattice

A network of hydrogen bonds

I now diverge from the path set by Ben-Naim and the MB model. I explore a model in which the particles are free to rotate but remain localized to the sites of the hexagonal lattice, for simplicity. First, it should be noted that the ground state is antiferromagnetic, in the sense that two arms from adjacent sites point in opposite directions (toward each other). However, the ground state becomes ferromagnetic by defining the orientations of all the sites in one triangular sub-lattice to be the opposite of where the arms point to. Also, in order to well-define the orientation of each site, its value should be limited to the range $(-\frac{\pi}{3}, \frac{\pi}{3}]$.

The energy of interaction between neighboring sites i and j is a function the orientations θ_i, θ_j, representing distortion of the hydrogen bond. The energy of distortion includes separated contributions from each site and a term for cooperative distortion. Calculating a coarse-grained orientation field $\theta(\boldsymbol{x})$, the Hamiltonian for small distortions can be written as

$$\beta\mathcal{H} = \int d^2\boldsymbol{x} \left[\frac{K}{2}(\nabla\theta(\boldsymbol{x}))^2 + \cdots - h\cos 3\theta(\boldsymbol{x})\right]$$

where the last term couples the field to the underlying hexagonal lattice.

The form of the Hamiltonian describes a mathematical phase transition. By applying the saddle-point approximation we get $-3h\sin 3\theta = 0$. The values of θ which minimize the integrand are

$$\theta_{min} = \begin{matrix} 0\ for\ h > 0 \\ \frac{\pi}{3}\ for\ h < 0 \end{matrix}$$

thus the value of θ_{min}changes discontinuously as h changes sign. However, the value of h is determined by the definition of θ, due to the physical coupling of the non-distorted hydrogen bonds to the lattice. Therefore, the system described by the Hamiltonian does not exhibit critical behavior. The long-range order of the ground state is destroyed in any finite temperature.

A different way of seeing this goes though calculating the pair-correlation function. For small deviations from the aligned state, the Hamiltonian could be written as

$$\beta\mathcal{H} = \int d^2\boldsymbol{x}\left[\frac{K}{2}\left(\nabla\theta(\boldsymbol{x})\right)^2 + \cdots - h\left(1 - \frac{9}{2}\theta(\boldsymbol{x})^2 + \cdots\right)\right]$$

The Fourier transform of the Hamiltonian is

$$\beta\mathcal{H}[\boldsymbol{q}] = \int \frac{d^2\boldsymbol{q}}{2\pi^2}\left[\frac{Kq^2}{2} + \frac{9h}{2}\right]|\theta(\boldsymbol{q})|^2$$

And the desired function is

$$\langle\theta(0)\theta(\boldsymbol{x})\rangle = \int \frac{d^2\boldsymbol{q}}{2\pi^2} e^{-iqx}\langle\theta(\boldsymbol{q})\theta(\boldsymbol{q}')\rangle = \int \frac{d^2\boldsymbol{q}}{2\pi^2}\frac{1}{Kq^2 + 9h}$$

The pair-correlation function does not diverge, since $h > 0$ by definition. Moreover, taking $h \to 0$ will not bring the system closer to criticality, since without a symmetry breaking term Goldstone modes will arise, preventing long range order. Of course, this case would be equivalent to the XY model, where topological defects may bring the system to a Kosterlitz-Thouless transition. In any case, $h \to 0$ does not describe the system in discussion.

Adding small hydrophobic particles to the system

According to LCW theory, the presence of small hydrophobic particles constrains the motion of nearby water molecules. However, the hydrogen bonds between these molecules remain in-tact. In the model that I explore the water-like molecules have only rotational degrees of freedom. Therefore, it makes sense to describe the effect of small hydrophobic particles as constraints on the rotational freedom of a few hydrogen-bonded molecules.

Following that line of logic, I make it an assumption of the model that one hydrophobic particle fixes n_w molecules in the aligned state $\theta = 0$. Denoting the concentration of small hydrophobic particles in the system as $c(\boldsymbol{x}) \ll 1$, I calculate the effect of c on the coarse-grained orientation field. In general, the field at position $\boldsymbol{x}$ is defined by averaging over a number n_l of lattice sites around $\boldsymbol{x}$

$$\theta(\boldsymbol{x}) = \tfrac{1}{n_l}\textstyle\sum_{i=1\ near\ x}^{n_l}\theta_i$$

To the lowest order in c, the chance to encounter one hydrophobic particle around $\boldsymbol{x}$ is

$$P(1,\boldsymbol{x}) = c(\boldsymbol{x})\left(1 - c(\boldsymbol{x})\right)^{n_l-1} = c(\boldsymbol{x}) + O(c(\boldsymbol{x})^2)$$

Similarly

$$P(0,\boldsymbol{x}) = \left(1 - c(\boldsymbol{x})\right)^{n_l} = 1 - n_l c(\boldsymbol{x}) + O(c(\boldsymbol{x})^2)$$

$$P(n,\boldsymbol{x}) = O(c(\boldsymbol{x})^2)\ for\ n \geq 2$$

The effect of $c(\boldsymbol{x})$ on the field is as follows

$$\begin{aligned}\theta(x)' = {} & \frac{\left(1 - n_l c(\boldsymbol{x})\right)\theta(\boldsymbol{x}) + c(\boldsymbol{x})\theta(\boldsymbol{x})\left(1 - \frac{n_w}{n_l}\right)}{1 - c(\boldsymbol{x})(n_l - 1)} \\ & + O(c(\boldsymbol{x})^2) \\ & = \theta(\boldsymbol{x})\left(1 - \frac{n_w}{n_l}c(\boldsymbol{x}) + O(c(\boldsymbol{x})^2)\right)\end{aligned}$$

Where I assumed that averaging over the $n_l - n_w$ orientations which are not affected by the hydrophobic particle gives the same value as averaging over all n_l orientations without the presence of the particle. The Hamiltonian takes the form

$$\begin{aligned}\beta\mathcal{H} = \int d^2\boldsymbol{x}\Bigg[& \frac{K}{2}\left(\nabla\theta(\boldsymbol{x})\right)^2 + \cdots \\ & - h\left(1 - \frac{9}{2}\theta(\boldsymbol{x})^2 + \frac{9n_w}{n_l}c(\boldsymbol{x})\theta(\boldsymbol{x})^2 \right. \\ & \left. + \cdots\right) + \frac{c(\boldsymbol{x})^2}{2\sigma^2}\Bigg]\end{aligned}$$

where all the interactions are calculated up to cubic terms. The last term describes van der Waals attraction among hydrophobic particles. It should be noted that vdW attraction between hydrophobic particles and water molecules is implicitly taken into account by not penalizing for distortion of hydrogen bonds near hydrophobic particles.

The contribution of $c(\boldsymbol{x})$ to the partition function can now be integrated out by "completing the square", resulting in an additional term which is proportional to $\theta(\boldsymbol{x})^4$ in the effective Hamiltonian. In order to avoid the calculation of quartic terms in the coupling of $c(\boldsymbol{x})$ to the field, I assume that $c(\boldsymbol{x}) \ll \theta(\boldsymbol{x})$. Therefore, the only quartic terms that appear in the effective Hamiltonian are proportional to $\theta(\boldsymbol{x})^4$

$$\begin{aligned}\beta\mathcal{H}_{eff} = \int d^2\boldsymbol{x}\Bigg\{ & \frac{K}{2}\left(\nabla\theta(\boldsymbol{x})\right)^2 - h\left(1 - \frac{9}{2}\theta(\boldsymbol{x})^2\right) \\ & - \left[\frac{9^2}{4!}h + \frac{1}{2}\left(\frac{9n_w h\sigma}{n_l}\right)^2\right]\theta(\boldsymbol{x})^4 \\ & + O(c(\boldsymbol{x})^2\theta(\boldsymbol{x})^2)\Bigg\}\end{aligned}$$

Some effects of the hydrophobic particles on the model can be probed by considering $\theta(\boldsymbol{x})$ in the saddle-point approximation. For the physical case $h > 0$, still $\theta_{min} = 0$. However

$$\theta_{max} = \tfrac{{n_l}^2}{18{n_w}^2\sigma^2 h}\left(1 + O\left(\tfrac{1}{{n_w}^2\sigma^2 h}\right)\right)$$

where I assumed that $h \gg 1$.

It is not entirely clear what information θ_{max} provides about the system, unlike the case of θ_{min}, which describes the ground state of the model. Nevertheless, in this case one can think about θ_{max} as describing high energy states of the system when there is no cooperative distortion of hydrogen bonds ($\nabla\theta = 0$). It should be noted that $\theta_{max} \to 0$ for certain values of the parameters $n_w{}^2, \sigma^2, h$, i.e. these values describe conditions in which all the hydrogen bonds are aligned even in the highest possible energy states. These conditions can be interpreted as a) strong coupling to the lattice $|h| \to \infty$, b) long-range effect of hydrophobic particles on the system $n_w \to \infty$ and c) a weak interaction among hydrophobic particles $\sigma \to \infty$. The last condition is not as intuitive as the others. By considering the Gaussian term that was integrated out, it is clear that the average of $c(\boldsymbol{x})$ is

$$\langle c(\boldsymbol{x})\rangle = \frac{9hn_w\sigma^2}{n_l}\theta(\boldsymbol{x})^2$$

Thus, it might be a corollary of the coupling of $c(\boldsymbol{x})$ to the field that when $\sigma \to \infty$ the field must vanish to keep $c(\boldsymbol{x})$ finite.

It must be reminded also that the model might not accurately predict the behavior of the coupling of $c(\boldsymbol{x})$ and $\theta(\boldsymbol{x})$ as the latter becomes very small. That is because when the assumption $c(\boldsymbol{x}) \ll \theta(\boldsymbol{x})$ is not satisfied, one should justify including the $\theta(\boldsymbol{x})^4$ contribution from the Gaussian integration without considering terms of order $c(\boldsymbol{x})^2\theta(\boldsymbol{x})^2$.

I stop at this point. The natural next step is taking the Fourier transform of the Hamiltonian and treat the quartic terms as a perturbation. However, that cannot be done, since one of the quartic terms shares a coefficient with a quadratic term. Therefore, threating this coefficient as a small parameter will affect the unperturbed Gaussian model. A cost-effective next step for examining the behavior of the model may be running a computer simulation. It would be interesting to see whether the presence of these hydrophobic particles causes a phase transition in the system at finite temperatures.

Conclusions

In this work I explored a model which aims to capture the constraining effect of hydrophobic particles on the entropy of a network of hydrogen bonds. The two dimensional system on a hexagonal lattice does not show critical behavior at finite temperatures despite the lack of continuous symmetry.

Based on LCW theory of the hydrophobic effect, I chose to model small hydrophobic particles as a concentration field which fixes local regions of the orientation field aligned with the lattice. The approximated coupling of the two fields produces long-range order in the system under extreme conditions.

More studies of this model can be done in order to understand the effect of this kind of "hydrophobicity" on the rotational degrees of freedom. Other aspects of the hydrophobic effect require theoretical description too. In particular, a theory for the behavior of a small number of water molecules close to hydrophobic surfaces with various curvatures would greatly aid the research of protein folding.

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