

# Ethanol and its effects on ice premelting

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April 6, 2008

## Abstract

Condensed phases of water have been studied computationally to explain recent experimental results and derive understanding of the liquid/solid interface. The temperature dependence of the thickness of the surface melting is not well established. To better understand the effect of contamination on the experimental results, a novel molecular dynamics study is proposed in order to study the effects of polar molecules on surface destabilization. Potential models for water and ethanol are discussed in relation to relevant studies, and the method of path integral molecular dynamics is proposed to recover quantum effects.

## 1 Background

Solid properties of water such as the low frictional coefficient and facile sintering have attracted not only ice skaters and snow ball fighters but scientific interest as well. Since at least 1850, scientists and engineers have been interested in properties of ice [1]. The lower density solidified of water even attracted British aircraft builders during World War II [2].

One property that has generated recent interest is the liquid-like layer present on the surface of ice at temperatures well below the freezing point [3,4]. This premelt layer has implications for a wide range of fields. In atmospheric chemistry, there are indications that the surface melt changes the reactive uptake coefficients, thereby altering predictions of ozone destruction [5,6]. A recent review of the range of environment consequences of this premelting is given in reference [7].

The formation of a pre-melting layer results from equilibrium effects that serves to lower the free energy of the surface at temperatures below the bulk melting point. This layer still shows properties of the underlying bulk that distinguish it from simply being the supercooled liquid phase [3,4]. This quasi-liquid layer has been observed in metallic solids, organic crystals and semi-conductors [3]. However, surface melting is dependent on the orientation of the crystal surface and not all surfaces exhibit pre-melting. It is believed that the onset of ice pre-melting is around 243K, however the temperature dependence of the thickness of the surface melt has not been unequivocally established [4]. Differences in reported thicknesses vary as much as two orders of magnitude at a given temperature [1,4]. This difference is attributed to two causes: differences in analytical techniques and the sensitivity of the pre-melt to experimental variables. Since the quasi-liquid layer is not the same as the bulk liquid nor the bulk solid, it is somewhat expected

that different experimental techniques will measure the thickness of the pre-melted layer differently [4, 7]. The second cause for the discrepancies is the sensitivity of experimental variables. The concentration of impurities is also thought to play a significant role in governing the thickness, suggesting that this may be a cause of experimental error [7, 8]; hence this proposed study.

To appreciate more fully the effects of impurities on the thickness of the pre-melt, a novel molecular dynamics study is proposed in which the solute is a polar ethanol molecule in contrast to ionic solutes already studied [9–11]. The adsorption of ethanol has been studied in both MD and DFT studies but the temperatures were low enough that surface of ice was not expected to show premelting destabilization [12, 13]. In this study, the effects of ethanol are to be studied in temperature ranges where premelting is a consideration.

## 2 Molecular Dynamics

Molecular dynamics is a viable method for studying liquids and is based on the integration of the classical equations of motion [14, 15]:

$$\dot{q} = \frac{\partial H}{\partial p} \quad \text{and} \quad \dot{p} = -\frac{\partial H}{\partial q}, \quad (1)$$

using an integration scheme such as the Verlet algorithm [14]. The applicability of classical mechanics is limited because classical mechanics is only an approximation to quantum mechanics. Due to the complications stemming from the Schrödinger equation, using classical equations of motion allow the treatment of much larger systems sizes. However, the drawbacks are that the quantum effects are not always negligible. The importance of the quantum effects in water simulations has been demonstrated by a variety of studies [16–18]. Most recently, and most relevant, Paesani and Voth [18], showed that quantum effects strongly modify the predictive ability of pre-melting phenomenon. Because ethanol-ice interactions are expected to occur mainly through the hydrogen of the hydroxyl group, the quantum description of the hydrogen is expected to be important in describing this interaction [13].

Two methods to circumvent these non-negligible effects are path integral molecular dynamics (PIMD) and modification of the models so that averaged quantum effects are included. In the latter case, example of modifications include making high frequency bonds rigid so that the bonds will not be excited in an unphysical way [14]. The creation of classical two-body potentials that better emulate quantum effects can be accomplished via a variety of approaches reviewed in reference [19]. Although important quantum effects can change the intermolecular potential energy by as much as nine percent [16], many of the features are adequately reproduced at a lower computational cost [20].

### 2.1 Path Integral Molecular Dynamics

The second option that allows recovery of quantum effects is the use of PIMD. The well known analog of Feynman’s path integral with the classical partition function can be used

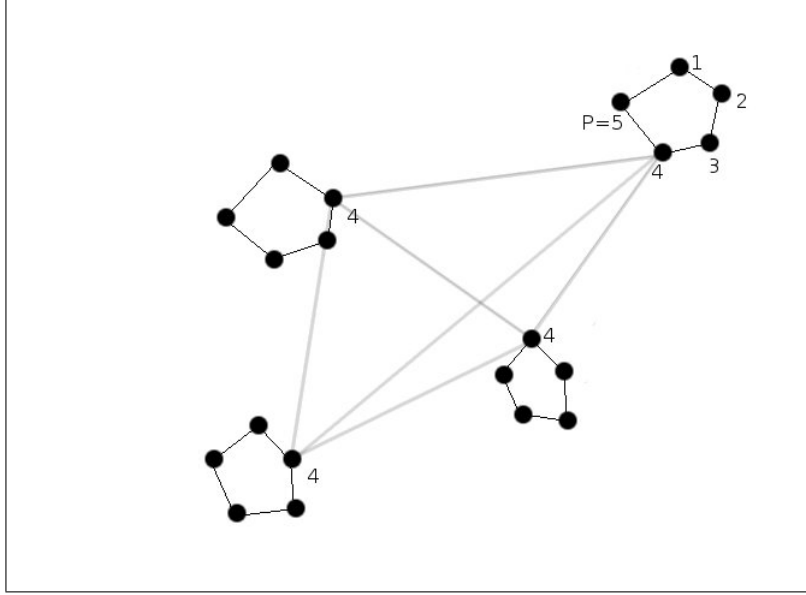


Figure 1: A system of four quantum particles is shown with  $P = 5$  pseudo-particles representing each particle. To illustrate the potential function of the system, the interaction between the 4th pseudo-particle of each particle is drawn in grey.

to recover quantum effects [21, 22]. The propagator of the path integral formalism [22],

$$K(x, t; x', t_0) = \int_x^{x'} \mathcal{D}x(s) e^{-\frac{i}{\hbar} \mathcal{A}[x(s)]},$$

can be related to the density matrix via the transform  $\beta = it/\hbar$ . After setting  $\beta = it/\hbar$  the density matrix is given by:

$$\rho(x, x') = \int_x^{x'} \mathcal{D}x(\tau) e^{-\frac{S[x(\tau)]}{\hbar}}.$$

Here,  $\tau$  is imaginary time,  $it$ , and the Euclidean action,  $S$ , is defined as:  $S[x(\tau)] = \int_0^{\beta\hbar} d\tau \mathcal{L}_E(x, \dot{x})$ . Here  $\mathcal{L}_E$  is the Euclidean Lagrangian which is the *sum* of the kinetic and potential energies. Given that the trace of the density matrix is the partition function,  $Z$ , we have:

$$Z = \int dx \int_x^x \mathcal{D}x(\tau) e^{-\frac{S[x(\tau)]}{\hbar}} = \oint \mathcal{D}x(\tau) e^{-\frac{S[x(\tau)]}{\hbar}}, \quad (2)$$

and the integration is over all closed loops  $x(\tau)$  such that  $x(0) = x(\beta\hbar)$ . When the partition function is actually evaluated via PIMD, a Trotter expansion must be used because the kinetic and potential operators do not, in general, commute. Using  $P$  Trotter points to divide the path integral for  $N$  quantum particles of masses  $\{M_I\}$  leads to the canonical partition function  $Z(N, V, T)$  given by:

$$Z(N, V, T) = \lim_{P \rightarrow \infty} \left[ \prod_{I=1}^N \left( \frac{M_I P}{2\pi\beta\hbar^2} \right)^{3P/2} \int_{D(V)} dR_I^{(1)} \dots dR_I^{(P)} \right] \\ \times \exp \left[ -\beta \sum_{i=1}^P \left( \sum_{I=1}^N \frac{1}{2} M_I \omega_P^2 (R_I^{(i+1)} - R_I^{(i)})^2 + \frac{V(R_1^{(i)}, \dots, R_N^{(i)})}{P} \right) \right]. \quad (3)$$

For each of the  $N$  particles there are  $P$  pseudo-particles which are actually moved during the MD simulation according to (3). To make the connection to MD apparent let  $U_{eff}$  be defined as the argument of the exponential and introduce  $P^N$  arbitrary Gaussians into (3) and the appropriate constant,  $\mathcal{N}$ . This leads to:

$$\begin{aligned} Z(N, V, T) &= \lim_{P \rightarrow \infty} \mathcal{N} \prod_{I=1}^N \int dR_I^{(1)} dP_I^{(1)} \dots dR_I^{(P)} dP_I^{(P)} \exp \left\{ -\beta \left( \sum_i \frac{(P_I^{(i)})^2}{2\tilde{m}_I^{(i)}} + U_{eff} \right) \right\} \\ &= \mathcal{N} \int dR_1^{(1)} dP_1^{(1)} \dots dR_N^{(P)} dP_N^{(P)} \exp \left\{ -\beta \sum_{I=1}^N H_{eff}^{(I)} \right\} \end{aligned} \quad (4)$$

The effective Hamiltonian of the  $P^N$  pseudo-particles with effective masses  $\{\tilde{m}\}$  can then be used to derive the equations of motion according to (1). A normal mode transformation or a staging transformation can be used to ensure that the full phase space is sampled [21]. As in typical MD simulations, the canonical distribution is accomplished by thermostating the systems using a techniques such as the Nosé-Hoover chain [23]. Because of the dominant harmonic forces, a thermostat must be coupled to each degree of freedom [21] and a chain of length of four was used in reference [24].

## 2.2 Potential Model

The last topic to be discussed regarding the proposed MD implementation is the potential model of the water and the solute. There are many model potentials available for the simulation of water [19]. The model potentials may be designed for simplicity and ease of implementation [25], or parametrized to reproduce specific properties [20, 26], or parametrized according to *ab initio* data [27].

Most water potentials are rigid planar representations, although notable exceptions include the atom-atom potential of reference [9, 10]. The popular rigid non-polarizable TIP4P model contains four interaction sites has been updated to reproduce the condensed properties of water as TIP4P/2005 [20, 28]. TIP4P/Ice was parametrized specifically so as to reproduce experimental properties of ice [29]. The use of PIMD in the TIP4P model has shown 35 K temperature shifts of the mechanical melting temperature [24], further indicating the need to go beyond MD when using this model. One open question that should be addressed is how well the properties of ice will be reproduced if PIMD is used instead of MD with the specifically parameterized TIP4P/Ice. This investigation of the TIP4P/Ice may glean insight on how to better parameterize the models for use in PIMD and will provide useful information about the model itself.

An alternative to fitting a water model to experimental data, is a route that fits parameters according to high level *ab initio* data. The Thole-type [30], polarizable flexible interaction model (TTM2.1F) [27] has been tested in a wide range of classical and quantum simulations [17, 18, 27, 31]. Most importantly, surface melting has been examined using this model [18]. Recovering the original results provides a confirmation for the computational implementation before the testing of ethanol's effect.

The potential of the solute must also be addressed. The basis for the TIP4P model, the transferable intermolecular potential (TIP) has specified parameters for simulating ethanol as well [26, 28]. A previous study of the adsorption of ethanol on ice in atmospheric conditions lists a set of MD parameters to describe the ethanol-ethanol interaction [12].

Many of the popular force fields such as CHARMM already include parameters for ethanol but these are usually not polarized [32, 33]. Polarizability of the ethanol can be taken into account using auxiliary Drude particles attached to each heavy atom [34]. These Drude particles carry a partial charge and oscillate classically via an extended Lagrangian [35]. This method was created for use in MD and extensions to PIMD may prove to be enough for a completely separate project but, nonetheless, provides a starting point for the addition of polarizability. Because the TTM2.1F model of water is polarized, the polarizability (or lack thereof) of the ethanol molecules will likely play an important role. Finally, combining the descriptions of the interactions between the ethanol and water is typically accomplished using the Lorentz-Barthelot rules [12, 36].

### 3 Ice Modeling

In order to simulate the effects of ethanol concentration on premelting, it is important to establish a working model of ice. Ice has several phases but it is nearly always found in the Ih form at terrestrial conditions [37]. Ih, or hexagonal ice, is characterized by a hexagonal lattice in a proton disordered state. The so called ice rules are derived from the following information: (1) there is only one proton on each bond and (2) there are two protons near each oxygen [38]. The dipole moment should be minimized by following these rules and provides a check that the protons are configured randomly. Classical simulation can be used to obtain the starting geometry of the ice [24]. Also, since the surface melting is not isotropic, different surfaces of the ice must be tested separately.

Like all computational work, MD has its computational limitations. First, consider the length of the simulation. Typically, femtosecond timesteps are used to generate trajectories of tens of nanoseconds [14, 21]. Since dynamics quantities are not being considered, the length of the trajectory should be sufficient provided that the initial configuration is reasonable. Second, MD is limited in the number of molecules that can be considered. To circumvent this periodic boundary conditions are imposed. When this is done, the long range electrostatic interactions can be handled via a cutoff [11] or considered using the Ewald summation method [14]. Within the repeated cell, thousands of water molecules can be simulated classically [9–11], whereas far less can be done using PIMD. PIMD requires more computational effort and is limited to hundreds of molecules [18, 24, 31]. Moreover, the number of molecules considered must be balanced with the number of pseudo-particles representing each molecule. The number of pseudo-particles used affects how accurately the quantum effects will be recovered. With the TIP4P model,  $P = 5$  is seen to be sufficient [24], and it can be expected that a similar value should hold for other TIP4P-like models. Using the TTM2.1F model,  $P = 32$ , has been shown to be sufficient [17, 18, 31]. It should be noted that the TTM2.1F model has been designed for parallel implementations offering the hope of extending the number of molecules and pseudo-particles possible.

Several interesting observations can be made from this simulation. First, in the study of ions on the surface premelt, it is observed that the ions remain close to the surface and that their mobility is dependent on the thickness of the quasi-liquid layer [11]. Second, the preferred orientation of the ethanol can be compared with a density functional study carried out at a much lower temperature [13]. Finally, the changes in the solvation shell

of ethanol will be interesting to observe within the thin layer of liquid.

To examine the disorder of the ice surface, reference [18] suggests the local translational order parameter. It is given by:

$$S_T = \frac{1}{3N_L^2} \sum_{m=1}^3 \sum_{i=1}^{12} \sum_{j=1}^{12} \cos(\mathbf{k}_m \cdot \mathbf{r}_{ij}). \quad (5)$$

Here  $\mathbf{k}_1 = 2\pi/a(1, 1/\sqrt{3}, 0)$  and the other two  $\mathbf{k}$  vectors are related by  $120^\circ$ .  $N_L$  is the number of water molecules located in each layer and  $\mathbf{r}_{ij}$  is the vector pointing from oxygen atom  $i$  to oxygen atom  $j$  in a given layer and  $a$  is the lattice constant of the basal plane. As the surface becomes disordered the value of the order parameter is  $1/N_L$  and for the perfect lattice it is 1. After equilibrating at each temperature, the effects of ethanol on ice can be quantified numerically using this order parameter. There are other order parameters that can be used and in the course of the study other order parameters may prove useful.

## 4 Proposed Work

The major goals of the proposed work are: (1) test models of ethanol and water interactions, (2) examine the equilibrium concentration profile of the ethanol in the pre-melt, and (3) compare the thickness of the pre-melt layer with and without ethanol present.

The first of the goals involves testing various model of ethanol and water and the combinations of them. To narrow the focus of the study, only the TTM2.1F would be used for the water. The ethanol parameters must be more systematically approached beginning with the parameters listed in the previous studies mentioned in section 2.2. Since these parameters are designated for use in MD some simple modifications may be pursued to obtain better results using PIMD. The metric of the interactions is the recovery of low temperature ice-ethanol interaction consistent with DFT studies and recovery of reasonable the water-ethanol interactions as compared to older studies.

Once an approximate model of the system is established, the concentration profile of the ethanol at equilibrium would be the first piece of data to be gleamed. This is interesting because it is can be compared to the ionic cases studied and provide preliminary results about polar molecules in the pre-melt.

Finally and most importantly, the effect of ethanol on the thickness of the pre-melt at temperatures below the bulk melting temperature is to be examined. The positive results of the first two stages of this work will allow some confidence to be made about conclusions drawn about the effect on the surface melt. The idea of studying the ethanol-water interactions is born out of the experimental discrepancies and hopefully this set of MD studies can provide insight about the effect of polar rather than ionic solutes on the ice surface. Unfortunately, the use of PIMD means that no dynamics can be recovered, therefore the establishment of equilibrium order parameters is crucial and an obvious extension of this work is going beyond the local translational order parameter to other order parameters.

## 5 Acknowledgement

Thank you to professor Aspuru-Guzik for the freedom to pursue this tangent. The author would also like to thank professors E. Shakhovich, B. Bagchi, and M. Carignano for thoughtful input. Finally, I must acknowledge my fellow group members for listening to my tirades on melting.

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