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Thermodynamics of stacking disorder in ice nuclei

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A simple Ising-like model for the stacking thermodynamics of ice 1 is constructed for nuclei in supercooled water, and combined with classical nucleation theory. For relative stabilities of cubic and hexagonal ice I within the range of experimental estimates, this predicts critical nuclei are stacking disordered at strong sub-cooling, consistent with recent experiments. At higher temperatures nucleation of pure hexagonal ice is recovered. Lattice-switching Monte-Carlo is applied to accurately compute the relative stability of cubic and hexagonal ice for the popular mW model of water. Results demonstrate that this model fails to adequately capture the relative energetics of the two polytypes, leading to stacking disorder at all temperatures.

I. INTRODUCTION

Formation of ice 1 from supercooled water is the archetypal crystal nucleation and growth problem. Ice 1 can exist in cubic (ABCABC stacking) and hexagonal (ABABAB stacking) polytypes, denoted as ice 1c and ice 1h respectively. Both consist of identical double-layers of ice molecules which can adopt either a positive or negative transverse shift relative to the previous double-layer. In practice, ice 1h is normally grown in simple freezing experiments. At stronger supercooling, ice with a large proportion of cubic-like stacking faults is formed1.

Atomic simulations of ice nucleation are hampered by the extremely long timescales required to sample even a single nucleation event in a tractable simulation volume. Brute-force simulation methods have only succeeded in freezing bulk water when using aggressively truncated model potentials2 or in the presence of electric fields3, where nucleation barriers are very much reduced. Adoption of coarse-grained models4,5 and/or rare-event sampling methods6–10 can alleviate this problem. However no simulation study of ice nucleation has observed formation of pure ice 1h at any temperature without imposing favourable boundary conditions11, or starting from a hexagonal crystal seed12.

II. STACKING MODEL

Following earlier work on fcc/hcp polytypism in hard spheres13,14, finite stacking sequences can be mapped onto an equivalent 1-dimension Ising-like system. The label $S_i$ (A, B or C) denotes the shift of the $i^{th}$ double-layer relative to an arbitrary origin. Periodicity requires that three consecutive shifts in the same direction return a layer to its original position, and hence cyclic permutation of the labels A, B and C leads to a redundant sequence.

Each layer of a finite stacking sequence $\{S_i\}$ can easily be identified as cubic or hexagonal by comparing the labels of its two nearest-neighbours. Double-layers with two identical neighbours contain hexagonally coordinated molecules, leading to a simple Hamiltonian:

$$H = -\delta g_{hc} \sum_{i=2}^{L-1} N_i \delta S_{i+1}, S_{i-1}$$

where $\delta g_{hc}$ is the Gibbs free energy difference per molecule between pure hexagonal and cubic polytypes, $N_i$ denotes the number of molecules in the $i^{th}$ double-layer and the Kronecker $\delta$ counts contributions from only hexagonally-stacked layers. This corresponds to the Ising model subject to an external field in the absence of any coupling between spins. Interactions beyond those involving three double-layers (six molecular layers) are therefore neglected. Throughout this manuscript a preference for hexagonal structure is represented by positive $\delta g_{hc}$.

The molecular double-layers of water molecules at the sequence-terminating ice surfaces expose identical structure to the surrounding liquid, regardless of their transverse shift. Hence at the level of this model, ice 1h and 1c ice nuclei have identical surface energies, resulting in a uniform shift in energy independent of stacking sequence, which we neglect.

For a nucleus of $N = \sum N_i$ molecules, it is computationally trivial to enumerate all non-redundant stacking sequences of a given length, leading to exact (if tedious) expressions for the corresponding partition function. From this one can compute the percentage of molecules in a nucleus that exist within cubically-stacked layers. This requires some consideration of nucleus shape, which is taken to be approximately spherical, consistent with calculations of the interfacial free energy at the basal, prism and (1120) faces15.

Experimental estimates for $\Delta G_{hc} = N_A \delta g_{hc}$, the Gibbs free energy difference per mole between the two polytypes, are obtained from the heat evolved $\Delta H_{hc}$ on transforming cubic ice to hexagonal ice. Measurements of $\Delta H_{hc}$ are varied. Several measurements span the range from 13 to 80 J mol$^{-1}$16–20. An explicit dependence on temperature from 40 J mol$^{-1}$ at 130 K to 75 J mol$^{-1}$ at

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170 K has been inferred from measurements on micrometer droplets deposited on cold substrates. Measurements of the cubic ice vapour pressure by Shilling et al. have been used to calculate $\Delta H_{hc}$ as lying between 125 and 185 J mol$^{-1}$, consistent with the 160 J mol$^{-1}$ measured by Sugisaki et al.

One source of variation in these figures is the range of methods by which ‘cubic ice’ is obtained from other ice phases, consistent with these samples actually representing stacking disordered ice with varying degrees of cubic content. It is therefore likely that most measurements underestimate $\Delta G_{hc}^4$.

These are rather small energy differences, however their effect on the structure of ice nuclei within above stacking model is dramatic. Figure 1 plots the average number of molecules within cubic ice-layers as a function of nucleus size and temperature using $\Delta G_{hc} = 50$ J mol$^{-1}$. Open circles denote the critical nucleus size predicted by CNT using $\gamma_{sl} = 33$ mJ m$^{-2}$ and $\Delta H_{fus} = 6.01$ kJ mol$^{-1}$. Small changes of gradient discernible within the hexagonally dominated region correspond to appearance of an additional layer in the model nucleus on increasing $N$.

![Figure 1: Average percentage of molecules in cubic layers within ice nuclei of size $N$ at temperature $T$ according to the stacking model described in the text with $\Delta G_{hc} = 50$ J mol$^{-1}$. Open circles denote the critical nucleus size predicted by CNT using $\gamma_{sl} = 33$ mJ m$^{-2}$ and $\Delta H_{fus} = 6.01$ kJ mol$^{-1}$. Small changes of gradient discernible within the hexagonally dominated region correspond to appearance of an additional layer in the model nucleus on increasing $N$.](image)

Covered from this simple stacking mode, it is instructive to quantify $\Delta G_{hc}$ for the model of water most commonly employed in recent ice nucleation studies.

### III. MW WATER MODEL

The mW model was introduced by Molinero and Moore. Each molecule is represented by a single particle which interacts with neighbours via two-body and three-body terms, the latter favouring tetrahedral coordination environments. In the absence of explicit hydrogen, ice 1c and 1h are directly analogous to diamond and lonsdaleite in tetrahedrally coordinated semiconductors. The melting temperature of this model has been quantified as $T_m = 274.6$ K.

The short ranged interactions in this model, coupled with a lack of explicit electrostatic interactions (eliminating the need for expensive Ewald summation), makes this model substantially cheaper to simulate than all-atom representations. It has hence proven popular for studies of ice crystallisation. Initial studies used large-scale molecular dynamics (MD) to study crystallisation via ‘brute force’ at 180 K close to the spinodal regime where nucleation events are rather frequent. The resulting ice was found to be stacking-disordered with hexagonal and cubic layers in a 2:1 ratio. Reinhardt and Doye conducted umbrella sampling at 200 K and observed predominantly cubic critical nuclei. They also observed that seed nuclei of either polytype resulted in persistence of that structure to larger length scales during growth.

In contrast to all-atom models, it has proven possible to quantify kinetics of ice nucleation in the mW model. Li et al. have presented a thorough study using Forward-Flux sampling, over a temperature range from 220 to 240 K. Critical nuclei were again observed to be stacking disordered, with cubic and hexagonal regions of equal abundance. The lowest experimental estimate of $\Delta G_{hc}$ leads to formation of 30% cubic nuclei at 240 K in the above stacking analysis. It is therefore likely that the mW model underestimates this property.

By neglecting any possible entropy difference between the two polytypes, Moore and Molinero have computed $\Delta G_{hc} = 0 \pm 30$ J mol$^{-1}$ at 180 K from MD simulations of their model. The above stacking model predicts nuclei of hexagonal ice are only possible at the upper end of this range. No study with this model has been able to observe unbiased nucleation of pure hexagonal ice crystallites, as would be expected at higher temperatures close to coexistence. All observations of stacking disorder at low temperature are therefore lacking a control simulation for meaningful comparison.

To accurately determine the value of $\Delta G_{hc}$ for mW, a series of lattice-switching Monte Carlo (LSMC) calculations have been performed. This method has been used to accurately quantify the difference in free energy between hexagonal and cubic close-packings in hard spheres and Lennard-Jones particles. LSMC...

[9] Li, et al.
[27] Moore and Molinero.
performs Metropolis Monte Carlo simulation in $N$ displacements $\{u_i\}$ relative to ideal/reference lattice positions $\{R_i^\alpha\}$ where $\alpha$ denotes the currently ‘active’ lattice, here either cubic ($\alpha = 1$) or hexagonal ($\alpha = 2$) ice. Calculations are performed in the isobaric-isothermal (NPT) ensemble, using a set of ideal lattice vectors arranged into a matrix $h_0^\alpha$ and corresponding displacements from these $\delta h$. The usual MC displacement and Parrinello-Rahman lattice moves are augmented with ‘lattice switch’ moves which swap the auxiliary variable $\alpha$. The switch preserves the relative coordinates $\{u_i\}$ and lattice vectors $\delta h$ but shifts the absolute system configuration between crystal structures.

It is convenient to define an order parameter

$$
\mu (\{u_i\}, \delta h) = \beta (E^1 - E^2) + \beta P (V^1 - V^2) - N \ln (V^1/V^2)
$$

where $E^\alpha$ and $V^\alpha$ are the energy and volume of the system evaluated when displacements of molecule positions and cell vectors are measured with respect to the ideal configuration of phase $\alpha$, $\beta$ is the inverse temperature and $P$ is the external pressure. Displacements which favour lattice 1 (2) exhibit negative (positive) $\mu$. Moves from $\alpha = 1$ (2) to $\alpha = 2$ (1) are accepted with probability $\max [e^{\mu}, 1]$ ($\max [e^{-\mu}, 1]$).

The relative stability $\Delta G_{hc}$ can be recovered directly by counting the number of samples obtained within each phase at equilibrium. In practice, ‘gateway’ states ($\mu \approx 0$), from which the switch move can be accepted, are infrequently sampled. To rectify this, a multicanonical weight function $\eta (\mu)$ is introduced as an energy penalty such that a flat (biased) histogram $P (\mu)$ is obtained.

As the ideal bias $\eta (\mu)$ is exactly the unknown $-k_B T \ln P (\mu)$, it must be constructed iteratively. In this work the range of $\mu$ visited by both phases at equilibrium is partitioned into 150 bins of non-uniform size, using smaller intervals close to $\mu = 0$ and following a geometric progression in width to larger values of $|\mu|$. Starting from $\eta_i = 0$ in each bin, a procedure similar in spirit to Wang-Landau sampling is performed. After each visit to bin $i$, $\eta_i$ is incremented by $k_B T \ln f$ where $f$ is initially 1.001 and the histogram $h_i$ is incremented by unity. Acceptance probabilities for all moves incorporate the bias. The histogram is monitored, and upon reaching $\min \{h_i\} > 0.95 h_i$, $f$ is reduced to $\sqrt{f}$ and the histogram reset to zero. After 15–20 iterations, the $\eta$ function is sufficiently converged to allow uniform sampling with no further refinement. Typically this procedure requires between 2 and $5 \times 10^7$ MC sweeps using eight walkers in parallel, using shared weight and histogram arrays. Following this refinement, a final simulation (again using 8 walkers) is conducted using static weights is plotted in figure 2. Convergence of $\Delta G_{hc}$ (extracted from the running estimate of $P (\mu)$) for a simulation using static weights is plotted in figure 3.

A weakness of the LSMC method is the requirement that the two simulated supercells contain equal numbers of molecules. For crystal structures such as ice, this leads to pairs of supercells with substantially differing shape for all but a very few magic numbers. Table I presents a series of LSMC calculations for the mW model at 200 K over a range of system sizes. For isotropic expansion to the thermodynamic limit, the leading finite-size correction to the Gibbs free energy is expected to vary in inverse proportion to the system size. In figure 4 lines of isotropic expansion connect system sizes at which the two simulation cells are of common shape. All lines cross $1/N = 0$ within $2 \text{ J mol}^{-1}$ of each other. Finite size error is therefore substantially larger than the statistical error in each individual calculation, but no larger than $\pm 1.5 \text{ J mol}^{-1}$ at the largest system size of 384 molecules.
TABLE I. Calculated relative free energies of cubic and hexagonal ice at 200 K. Note that the final pair of simulation cells are not crystallographically aligned with others in the table.

<table>
<thead>
<tr>
<th>( N )</th>
<th>( \Delta G / J \cdot mol^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{a, b, c}{\AA} ) (cubic)</td>
<td>( \frac{a, b, c}{\AA} ) (hexagonal)</td>
</tr>
<tr>
<td>48</td>
<td>13.2, 8.77, 12.4</td>
</tr>
<tr>
<td>64</td>
<td>8.77, 17.5, 12.4</td>
</tr>
<tr>
<td>96</td>
<td>17.5, 13.2, 12.4</td>
</tr>
<tr>
<td>16</td>
<td>8.77, 8.77, 6.20</td>
</tr>
<tr>
<td>128</td>
<td>17.5, 17.5, 12.4</td>
</tr>
<tr>
<td>64</td>
<td>12.4, 12.4, 12.4</td>
</tr>
<tr>
<td>216</td>
<td>18.6, 18.6, 18.6</td>
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<tr>
<td>48</td>
<td>13.2, 8.77, 12.4</td>
</tr>
<tr>
<td>384</td>
<td>26.4, 17.5, 24.8</td>
</tr>
<tr>
<td>360</td>
<td>21.9, 22.8, 21.5</td>
</tr>
</tbody>
</table>

FIG. 4. Gibbs free energy difference \( \Delta G \) between cubic and hexagonal ice in the mW model as a function of inverse system size. Symbol shapes (diamonds, squares and circles) are shared by pairs of system sizes connected by isotropic expansion lines. Remaining system sizes are plotted as triangles. The statistical error bar on individual points is smaller than the symbol size.

At 200 K, the value of \( \Delta G_{hc} \) for mW water is at least one order of magnitude smaller than the lowest experimental estimate, but favours hexagonal ice in the thermodynamic limit. Figure 5 demonstrates the consequences of this in the present stacking model. Stacking disorder is favoured over the entire range of sub-cooling and nucleus size, indicating that mW ice nuclei in quasi-equilibrium will always be stacking disordered.

A strong temperature dependence of \( \Delta G_{hc} \) could recover a preference for hexagonal nuclei at high temperature. To investigate this possibility, LSMC calculations have been performed over a range of temperatures from 180-240 K at \( N = 384 \). These yield an approximately linear increase in \( \Delta G_{hc} \) of 0.4 J mol\(^{-1}\) with every 10 K increase in temperature. Including this in the stacking model results in no discernible change to figure 5.

It is also possible that interactions involving more than three molecular double-layers contribute to the energetics of stacking. This has been tested explicitly for the mW model for \( N = 360 \) system size using LSMC to compute the Gibbs free energy (relative to ice 1h) of stacking sequences which contain, 1, 2 and 4 cubic layers. In each case the free energy deviates from that predicted by equation 1 by no more than 0.12 J mol\(^{-1}\), comparable to the statistical uncertainly in the LSMC calculations. Including additional terms corresponding to coupling of nearest-neighbour spins does not improve the fit.

IV. CONCLUSIONS

By combining a simple Ising-like treatment of stacking energetics in ice 1 with CNT, a purely thermodynamic argument has been presented for an increased tendency to form hexagonal over stacking-disordered ice nuclei with increasing temperature. Predictions are consistent with mid-range experimental estimates for the relative stability of cubic and hexagonal ice and recent studies on homogeneous freezing\(^5\). The mechanism by which cubic stacking faults in low temperature nuclei persist to macroscopic size, is yet to be firmly established.

Detailed calculations on the popular mW water model have demonstrated its failure to capture a realistic free energy penalty for formation of stacking disordered ice, suggesting many recent simulation studies are unrealistically biased toward formation of stacking disordered ice\(^5,7,8\), and that some refinement of this model are required before quantitative conclusions on nucleation of the two polytypes can be inferred.

Although demonstrated to be unnecessary in the case of the mW model, inclusion of interactions between larger numbers of ice layers (higher order terms in the expansion) will increase the value of \( \Delta G_{hc} \) and thus the model will favour the hexagonal stacking sequence over stacking-disordered ice. A recent study\(^9\) has demonstrated the failure of CNT to capture the theoretical estimate of \( \Delta G_{hc} \) for mW water, and that some refinement of the model is required before quantitative conclusions on nucleation of the two polytypes can be inferred.
sion of Mau and Huse\textsuperscript{13} may be required to capture realistic ice stacking energetics. Indeed work based on fits to diffraction data\textsuperscript{36,37} strongly suggests this to be necessary. LSMC calculations on more detailed molecular models\textsuperscript{38,39} may exhibit this trend. Such calculations are under way and will be reported in a future communication.

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