

Calculating  
Ice–Water Interfacial Free Energy  
by  
Molecular Simulation

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by

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## ABSTRACT

This study presents a calculation of the free energy of the ice–water interface using molecular simulation. The method used is an adaptation of the *cleaving method*, introduced by Broughton and Gilmer, and subsequently enhanced by Davidchack and Laird.

The calculation is direct in the sense that an interface is formed during the simulation: isolated ice and water systems are transformed, via a sequence of reversible steps, into a single system of ice and water in contact. The method is essentially computational, that is, it does not correspond to any possible physical experiment, since non-physical potential energies are introduced (and subsequently removed) during the transformation process.

The adaptation of the method to water presented significant challenges, notably the avoidance of hysteresis during the transformation, and the devising of an ‘external’ energy potential to control the position and orientation of water molecules.

The results represent the first direct calculation by simulation of the solid–liquid interfacial free energy for a model of a molecular (as opposed to atomic) system.

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. . . . But pardon, gentles all,  
The flat unraisèd spirits that hath dared  
On this unworthy scaffold to bring forth  
So great an object. Can this cockpit hold  
The vasty fields of France? Or may we cram  
Within this wooden *O* the very casques  
That did affright the air at Agincourt?  
O pardon, since a crookèd figure may  
Attest in little place a million,  
And let us, ciphers to this great account,  
On your imaginary forces work.

*Henry V, Prologue*

# CHAPTER I

## INTRODUCTION

### 1.1 The Importance of Interfacial Free Energy

Interfacial free energy is defined as the reversible work required to form a unit area of an interface, an ‘interface’ being any smooth two-dimensional area of surface contact separating bulk volumes of two distinct substances, or of two distinct phases of the same substance. Interfacial free energy is usually denoted by the symbol  $\gamma$ , and measured in  $\text{mJ m}^{-2}$ . It is a physical property of matter of fundamental interest in the physical and chemical sciences.

Of particular interest is the interfacial free energy of the solid and liquid phases of the same substance, denoted by  $\gamma_{\text{sl}}$ . It provides a measure of the natural physical barrier to the spontaneous emergence, and persistence or growth, of the co-existence of two phases, and therefore plays a significant role in determining the characteristics and rates of freezing and melting phenomena, such as nucleation and crystal growth [1].

$\gamma_{\text{sl}}$  can counteract the free energy benefit from localised freezing, hence it is only (a positive)  $\gamma_{\text{sl}}$  which can give rise to the phenomenon of metastable supercooling in liquids. The size of the ‘critical nucleus’, that is, the smallest volume of the solid phase within a liquid bulk which is stable, can persist and grow, is determined by  $\gamma_{\text{sl}}$ , in conjunction with the free energy difference between the two bulk phases (all three quantities being themselves, of course, dependent on the temperature).

For any particular substance,  $\gamma_{\text{sl}}$  is not, in general, a constant, but rather, a function of two variables representing the angular orientation within the crystal lattice of the exposed solid surface (assuming, for the moment, the interface to be

planar). Given this definition for planar interfaces, then any smooth, non-planar interface will have a well-defined orientation, and hence value of  $\gamma_{sl}$ , at each point, determined by the tangent plane to the interface at that point. Hence  $\gamma_{sl}$  for any such surface can be calculated as an integral over the surface of ‘planar’  $\gamma_{sl}$  values. In this way, the planar definition suffices to characterise  $\gamma_{sl}$ . We shall refer to the dependency of  $\gamma_{sl}$  on the orientation of the crystal lattice as the ‘anisotropy’ of  $\gamma_{sl}$ . This anisotropy influences the large-scale shape of crystals emerging from bulk liquid, and the morphology of dendritic growth [2].

In summary, the ability accurately to determine  $\gamma_{sl}$  and its anisotropy, either by experimental measurement or theoretical calculation is of considerable fundamental and technological interest.

## 1.2 Homogeneous Nucleation

$\gamma_{sl}$  is of critical importance in the theory of homogeneous nucleation. Homogeneous nucleation is the onset of a phase transition within a uniform bulk substance, that is, a phase transition which arises as a result of the molecular energetics of the substance itself, and the random fluctuations which naturally occur at the ambient temperature and pressure, unaided by any ‘seed’ such as foreign particles within the substance, or a rough edge at the boundary of the substance and its container.

For example, in the phase transition of water freezing into ice, homogeneous nucleation will not occur even at temperatures well below the 0°C freezing point. This is a paradox, since at any temperature below the freezing point, the solid phase is energetically favourable. In other words, the total free energy of the substance when it has all frozen to ice is lower than its free energy when it is all in liquid form. This means that the liquid phase below the freezing temperature is thermodynamically unstable, and will in time freeze into the thermodynamically stable state. However, in practice this does not happen, and so-called ‘supercooled’ water seems to be in a stable state over any observable timescale. If the water is free of impurities (such as particles of dust), and the sides of its container are clean and smooth, then the only way it can start to freeze is by homogeneous nucleation, and it is a matter of experimental observation that this does not occur even at temperatures well below 0°C. The precise value of the homogeneous nucleation point of water is not known, estimates varying between  $-40^{\circ}\text{C}$  and  $-70^{\circ}\text{C}$  [3].

Supercooled water is ‘meta-stable’ – theoretically unstable, but stable in practice due to the extremely low probability of any transition path occurring which would take it to its true stable state. In order for the water to freeze, the freezing must start somewhere, the spontaneous formation of a small volume of ice. The reason why this is unlikely to happen can only be understood by considering the interfacial free energy at the ice–water interface. Of course in a large volume of water, homogeneous nucleation can occur anywhere in the bulk, so even if it is unlikely at any particular site, the number of potential sites (of the order of  $10^{20}$ ) could still make it likely that homogeneous nucleation will occur somewhere. However, the probabilities are so small that even when factored over a large volume of water, the probability remains so small that it never occurs in practice.

For a volume of ice to form within bulk water, in addition to the creation of that volume, an area of interface where the ice is in contact with the water is also created. Below the freezing point, the ice phase is energetically favourable, so ice formation gives energy to the system. At the same time, the interface is energetically unfavourable, compared to either bulk phase, and so its creation takes energy from the system.

If the latent heat of freezing of ice is  $G$  (in units of energy per unit volume), and assuming the volume of ice to be spherical, then the energy given to the system for nucleation of a sphere of radius  $r$  is  $4/3\pi r^3 G$ . If the interfacial free energy of ice–water is  $\gamma$  (in units of energy per unit surface area), then the corresponding energy taken from the system is  $4\pi r^2 \gamma$ . So for small volumes of ice (any value of  $r$  less than  $3\gamma/G$ ), there is an energy cost to the nucleation process. The exact shape of the ice crystal is not important, whatever the shape, the cost of creating the interface is proportional to the surface area of the interface, and the benefit is proportional to the volume, so there will always be a critical volume below which the nucleation event is unstable. Once the ice volume exceeds this critical volume, it becomes stable, and will grow, but any smaller volumes are unstable, and in the (statistically unlikely) event that they form at all, they will (very probably) melt again before attaining critical volume. It is therefore the interfacial free energy, which explains the barrier to homogeneous nucleation, and the metastability of supercooled water.

## 1.3 Calculation of Interfacial Free Energy

### 1.3.1 Experimental Measurement

The experimental measurement of solid–liquid interfacial free energies for any material is a significant challenge. Because of its importance, numerous experimental attempts have been made to determine the value for ice–water using a variety of methods. A review of the experimental results can be found in [4].

The diversity of experimental methods available has been accompanied by a commensurate diversity in the results obtained, with scatter in excess of 50%. Nevertheless, something approaching a consensus has emerged in recent years. Using a method based on observation of the shape of the grain boundary groove [5], Hardy obtained the value  $29.1 \pm 0.8 \text{ mJ m}^{-2}$  in 1977. Many of the more recent estimates are in reasonable agreement with that figure, for example, a Cahn-Hilliard analysis of nucleation data [4] has provided an estimate of  $27.1 \pm 0.2 \text{ mJ m}^{-2}$  and supercooling measurements [6] give an estimate of  $28 \pm 0.8 \text{ mJ m}^{-2}$ .

### 1.3.2 Calculation by Simulation

There are no (known) theoretical techniques for calculating  $\gamma_{\text{sl}}$ , the phenomenon seems too complex for direct theoretical attack. Hence the development and application of computational numerical techniques has become an important tool in evaluating interfacial free energy.

Since the 1970s, molecular simulations have been used in the calculation of  $\gamma_{\text{sl}}$ , and its anisotropy, though due to the limitations of computer hardware, and of available methodologies, much of the earlier work was performed on relatively simple theoretical systems such as hard spheres or Lennard-Jones spheres.

The development, over the past 30 years, of more powerful free energy methods, and of the computer hardware on which they rely, have enabled molecular simulation to become a realistic tool for calculation of accurate estimates of  $\gamma_{\text{sl}}$  for some real simple molecular systems, such as water (‘simple’ in this context referring only to complexity of molecular structure), though the quantity of published results in this field remains limited.

To our knowledge, the only previous attempt to determine  $\gamma_{\text{sl}}$  for the ice–water interface by computer simulation was by Haymet, Bryk, and Smith [7] for the SPC/E model of water. In that work, the surface *tension*, rather than interfacial free energy,

of the ice  $I_h$ -water interface was calculated along the basal face. It was argued that the difference between the tension and the free energy of the ice-water interface should be small, though the degree of approximation remains uncertain; tension and free energy coincide for liquid-liquid and liquid-vapor interfaces, while for interfaces involving solids, the two quantities may differ due to the ability of solids to support stress. The value in this case was determined to be  $39 \pm 4 \text{ mJ m}^{-2}$ , significantly higher than the experimental consensus discussed in Section 1.3.1 (page 4), and than our results reported here.

As regards computation of surface free energy itself (rather than tension) for the ice-water interface, two complementary computational molecular methods have been developed: the *cleaving method*, introduced by Broughton and Gilmer [8] and subsequently enhanced by Davidchack and Laird [9, 10, 11], and the *capillary fluctuation method* (CFM) proposed by Hoyt, Asta, and Karma [12]. The cleaving method uses external potentials to reversibly transform two separate solid and liquid systems prepared at coexistence conditions into a single system with the two phases juxtaposed to create an interface. The value of  $\gamma_{sl}$  is obtained directly by measuring the work performed by the external potentials during the transformation process. The main technical difficulty with this method is that it involves several stages, each of which requires precise control to ensure the transformation proceeds reversibly. The implementation of CFM is more straightforward, since it only requires the simulation of an equilibrated interfacial system. However, in this case the value of  $\gamma_{sl}$  is obtained indirectly, relying on the validity of the relationship between the magnitude of the capillary fluctuations and the *stiffness* of the interface, which, in turn, is related to  $\gamma_{sl}$  through a functional dependence with a carefully chosen set of anisotropy parameters. The cleaving method is more precise in determining specific values of  $\gamma_{sl}$ , while the CFM is more sensitive for ascertaining the anisotropy.

CFM is a well established method for cubic (e.g. fcc or bcc) crystals, but it does not lend itself so well to hexagonal crystal structures such as ice [13]. Also, since CFM relies on the *fluctuation* of the shape of the interfacial region, it can not be used for faceted interfaces, such as the interface at the ice basal plane, which do not fluctuate. Since the aim of our project was to calculate  $\gamma_{sl}$  as accurately as possible for the basal, prismatic and  $\{11\bar{2}0\}$  faces, the cleaving method was the natural choice.

We needed to make significant modifications to this method for it to be applied to water, since this is the first application of the method to a molecular system, or more

precisely to a system in which the molecular geometry is complex enough as to render a straightforward application of the original cleaving wall method inappropriate. Previous applications to molecular systems have not required such modifications, for example succinonitrile (SCN) [14] which freezes into an orientationally disordered bcc crystal and hence behaves essentially as atomic, and a hard-dumbbell system [15] to which the original hard-sphere cleaving walls approach [9] is directly applicable.

These modifications, described in detail in Chapter 4 (page 44), now enable the direct calculation of the solid-liquid interfacial free energy for *molecular* systems (though only water has been used in this work). The main challenge was to incorporate the orientational degrees of freedom into the transformation path, so that, in the process of forming the interface, the liquid molecules occupy crystal sites with appropriate orientational order. Even though the ice  $I_h$  structure consists of orientationally disordered hydrogen bonds, the orientation of molecules during the cleaving process needs to be controlled in order for the crystal structure to obey the Bernal-Fowler ice rules [16]: each molecule is involved in four hydrogen bonds, two acceptors and two donors. To achieve this, we devised a cleaving potential that influences both position and orientation of the molecules. This potential is generic in the sense that it can be applied to all types of rigid molecules, as well as being adaptable to flexible molecular systems. Using this new method, we have determined the free energy of the interface between ice  $I_h$  and water at ambient pressure for the basal, prismatic and  $\{11\bar{2}0\}$  orientations, repeated for three variants of the 4-site water model TIP4P.

## 1.4 Simulations Performed

The method was repeated with various different water models, as summarised in Table 1.1. Chapter 5 (page 66) presents a detailed discussion of the method and results for the truncated model. The procedure for the Ewald Sums models was somewhat more elaborate, partly due to enhancements we made in the light of our earlier experiences with the truncated model, and partly due to the additional techniques we developed to mitigate the additional computational demands of using Ewald Sums. The details for the Ewald Sums models are covered in Chapter 6 (page 71).

| <b>Model</b> | <b>Long-range forces</b>                                                            | <b>Thermostat</b> |
|--------------|-------------------------------------------------------------------------------------|-------------------|
| TIP4P        | Discontinuous cutoff at 10Å                                                         | Nosé-Hoover       |
| TIP4P        | Ewald Sums, real cutoff at 8.5Å, $\alpha = 0.26/\text{\AA}$ , $k = 1.15/\text{\AA}$ | Langevin          |
| TIP4P-Ew     | Ewald Sums, real cutoff at 8.5Å, $\alpha = 0.26/\text{\AA}$ , $k = 1.15/\text{\AA}$ | Langevin          |

Table 1.1: A summary of the models and their parameters studied for this work

# CHAPTER II

## SIMULATION ALGORITHMS

### 2.1 Molecular Dynamics

Since interfacial free energy is determined by the molecular structure of the materials, the only (known) way of calculating an estimate of its value computationally is by simulations at the molecular level. There are two well established approaches to molecular simulation: the Monte Carlo method and Molecular Dynamics.

The Monte Carlo technique evolves the spacial configuration of a system in a random manner, but in such a way as to ensure that the system represents reality in the sense that it provides (in the limit) correct statistical sampling of the thermodynamic ensemble. This is achieved by the use of (non-random) rules, which disallow some of the (random) moves based on the likeliness of the resulting spacial configuration.

The Molecular Dynamics technique approximates the time evolution of the spacial molecular configuration of a system. This is achieved by (approximately) solving the equations of motion of the system. Unlike Monte Carlo, the evolution of the simulation approximates the physical molecular motions over time. Like Monte Carlo, the system correctly samples the thermodynamic ensemble in the limit of increasing simulation time (for an ergodic system).

Either Monte Carlo or Molecular Dynamics methods would be suitable for the interfacial free energy problem, since interfacial free energy is a property of a system in an equilibrium state, and does not depend on dynamics. For this work, Molecular Dynamics was chosen, which is the method used in previous applications of the cleaving wall method.

## 2.2 Molecular Potentials

### 2.2.1 The Lennard-Jones Potential

Two neutral molecules, at sufficient distance of separation  $r$ , are attracted to each other. This attraction, known as the *van der Waals* force, is due to the dispersion of charge within each molecule. It decays as  $r^{-6}$ , as can be theoretically derived from, say, density functional theory.

At shorter ranges, a repulsive force dominates. This force, known as *Pauli exclusion*, is due to the overlap of charges occurring as the molecules approach each other. Its decay rate can not be derived theoretically, but it is often approximated by a decay as  $r^{-12}$ , mostly for computational efficiency, though other powers are also used in some model potentials.

The Lennard-Jones potential provides a model for these interaction forces. It takes the form:

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (2.1)$$

where  $r$  is the (scalar) distance between the atoms.

The parameters  $\sigma$  (the distance of separation at which the potential is zero), and  $\epsilon$  (the minimum value of the potential, at distance  $2^{1/6}\sigma$ , beyond which the force becomes attractive) are adjusted to fit the required molecule.

### 2.2.2 The Coulombic Potential

This takes the form:

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}, \quad (2.2)$$

where  $\epsilon_0$  is the permittivity of free space,  $q_1$ ,  $q_2$  are the two charges, and  $r$  is the (scalar) distance between them.

### 2.2.3 Truncation and Ewald Sums

In a simulation with periodic boundary conditions, the total force on a molecule is an infinite sum, since a molecule interacts not only with all the other molecules in the system, but also their periodic images. Since the sum has no analytic closed form,

some finite approximation is required for computation. There are two approaches to this approximation.

The first approach is to neglect any interactions at a distance greater than some ‘cutoff distance’,  $r_{cut}$ . If the cutoff distance is less than half the smallest dimension of the simulation cell, then only one image (the ‘nearest image’) of any molecule is in range. This approach is known as truncation, using the nearest image convention. Since many of the terms in the sum derive from long range coulombic interactions, decaying as  $1/r$ , the truncation approach, while simple and fast, may lead to significant loss of accuracy.

The second approach is to transform the coulombic sum into one whose terms decay exponentially with distance, using a technique known as Ewald Sums. The transformed sum can then be truncated with much smaller loss of accuracy. The approach is slower, but more accurate, than direct truncation of the coulombic sum. The mathematical treatment of Ewald Sums is covered in Chapter 6 (page 71).

Truncation can be discontinuous, in which case the potential is multiplied by a simple discontinuous cutoff function:

$$f(r) = \begin{cases} 1 & \text{if } r < r_{cut}, \\ 0 & \text{if } r \geq r_{cut}. \end{cases} \quad (2.3)$$

Such a discontinuous cutoff is sometimes used in Monte Carlo methods, but generally leads to numerical errors in molecular dynamics simulations, since numerical integration methods typically require some degree of continuity of the integrated functions. These numerical errors can lead to observable drift in temperature, but even if temperature is controlled by a thermostat, subtle anomalies can still arise, as discussed in Section 2.5 (page 22).

To avoid a discontinuity in the force at the cutoff radius, the cutoff function  $f(r)$  of Eq. (2.3) can be replaced by a smoothing function, which reduces the potential smoothly to zero as cutoff is approached. The smoothing function is usually a polynomial, for example, the following function gives a continuously differentiable potential:

$$f(r) = \begin{cases} 1 & \text{if } r \leq r_{mod}, \\ 2x^3 - 3x^2 + 1 & \text{if } r_{mod} < r < r_{cut}, \text{ where } x = \frac{r-r_{mod}}{r_{cut}-r_{mod}}, \\ 0 & \text{if } r \geq r_{cut}. \end{cases} \quad (2.4)$$

The function incorporates a cubic polynomial with coefficients chosen such that it smoothly descends from 1 to zero over the ‘cutoff band’  $[r_{mod}, r_{cut}]$ , and has zero gradient at both end-points of this interval. The system potential, rather than suddenly being cut off at  $r_{cut}$ , is now cut off gradually over the interval  $[r_{mod}, r_{cut}]$ . The precise value for  $r_{mod}$  is an arbitrary choice, it just needs to be somewhat less than  $r_{cut}$ . For this work, we used  $r_{mod} = 0.95r_{cut}$ .

The new potential,  $u_{cut}$ , is now defined in terms of the original potential,  $u$ , as follows:

$$u_{cut}(r) = u(r)f(r).$$

The corresponding force has magnitude  $F_{cut}$ , where:

$$F_{cut}(r) = \begin{cases} -u'(r) & \text{if } 0 < r \leq r_{mod}, \\ -u'(r)f(x) - u(r)\frac{6x(x-1)}{r_{cut}-r_{mod}} & \text{if } r_{mod} < r < r_{cut}, x = \frac{r-r_{mod}}{r_{cut}-r_{mod}}, \\ 0 & \text{if } r \geq r_{cut}, \end{cases}$$

and is directed in the line joining the interaction sites.

This new potential and its corresponding force are both everywhere continuous. The smoothing function defined by Eq. (2.4) was used throughout this work; higher order polynomials are also sometimes used to further increase the smoothness of the potential function [17].

## 2.3 Rigid Bodies

### 2.3.1 Treatment of rigid bodies in Molecular Dynamics

Throughout this work, water molecules are treated as rigid bodies. This approximation to the true physical situation is commonly used in molecular dynamics simulations.

To model a rigid body, there are two common approaches. One possibility is to use an atomistic algorithm, treating each atom composing the rigid body as free and independent, and then as a second stage in the time step, impose the rigid body structure by adjusting the atomic positions using a bond constraint algorithm (such as SHAKE / RATTLE). The second is to use a rigid body dynamics algorithm, in

which all the forces on the body are combined into a linear force and a torque which act on the motion of the body as a whole.

Many models of water contain interaction sites which are positioned away from any of the atoms. It is inappropriate to use a bond constraint algorithm in such a model, since the interaction sites which have no mass would have undefined acceleration if allowed to move independently. Therefore a rigid body dynamics algorithm is the natural choice for such models of water.

### 2.3.2 Equations of Motion in Quaternion Form

We chose an algorithm based on the quaternion formulation of rigid body dynamics, developed by Miller, Eleftheriou, Pattnaik, Ndirango, Newns and Martyna [18], in which the unit quaternion  $\{q_0, q_1, q_2, q_3\}$  with  $\sum_i q_i^2 = 1$  is introduced to define the orientation of the rigid body.

In the classical mechanics of rigid body motion, a rotation matrix is introduced to transform between body-fixed and space-fixed coordinates:

$$\begin{aligned}\mathbf{r}^b &= \mathbf{A}\mathbf{r}^s, \\ \mathbf{r}^s &= \mathbf{A}^\top \mathbf{r}^b,\end{aligned}\tag{2.5}$$

where  $\mathbf{r}^s$  (respectively  $\mathbf{r}^b$ ) denotes the coordinates of any ‘site’ on the molecule (with respect to its centre of mass) in the space-fixed (respectively body-fixed) coordinate system. Note that the rigid body is assumed to consist of a discrete number of point mass sites, as is the case for all of the water models we will be using. The body-fixed coordinate system is chosen so that the moment of inertia tensor,  $\mathbf{I}$ , defined by:

$$\mathbf{I}_{\alpha\beta} = \sum_{k=1}^N m_k (|\mathbf{r}_k|^2 \delta_{\alpha\beta} - \mathbf{r}_{k\alpha} \mathbf{r}_{k\beta}),\tag{2.6}$$

is diagonal. In the above equation, the sum is over the  $N$  sites of the body,  $m_k$  is the mass of site  $k$ , and  $\alpha, \beta$  are spacial coordinates.

The rotation matrix  $\mathbf{A}$ , expressed in terms of the quaternion  $\mathbf{q}$  is:

$$\mathbf{A}(\mathbf{q}) = \begin{pmatrix} q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2(q_1q_2 + q_0q_3) & 2(q_1q_3 - q_0q_2) \\ 2(q_1q_2 - q_0q_3) & q_0^2 - q_1^2 + q_2^2 - q_3^2 & 2(q_2q_3 + q_0q_1) \\ 2(q_1q_3 + q_0q_2) & 2(q_2q_3 - q_0q_1) & q_0^2 - q_1^2 - q_2^2 + q_3^2 \end{pmatrix}.\tag{2.7}$$

Note that the quaternion  $\mathbf{q}$ , and the rotation matrix  $\mathbf{A}(\mathbf{q})$  can also be expressed in terms of Euler angles [18]. The quaternion representation, being nonsingular (unlike the representation in terms of Euler angles), is more convenient, and generally preferred, for computational purposes.

Using the quaternion representation, the rigid body equations of motion are:

$$\begin{aligned}\dot{\mathbf{q}} &= \frac{1}{2}\mathbf{S}(\mathbf{q})\omega^{(4)}, \\ \dot{\omega}_x &= \frac{\tau_x}{I_{xx}} + \frac{(I_{yy}-I_{zz})}{I_{xx}}\omega_y\omega_z, \\ \dot{\omega}_y &= \frac{\tau_y}{I_{yy}} + \frac{(I_{zz}-I_{xx})}{I_{yy}}\omega_z\omega_x, \\ \dot{\omega}_z &= \frac{\tau_z}{I_{zz}} + \frac{(I_{xx}-I_{yy})}{I_{zz}}\omega_x\omega_y,\end{aligned}\tag{2.8}$$

where  $\omega_x, \omega_y, \omega_z$  are the body-fixed angular velocities,

$$\omega^{(4)} = \begin{pmatrix} 0 \\ \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}, \quad \mathbf{S}(\mathbf{q}) = \begin{pmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & -q_3 & q_2 \\ q_2 & q_3 & q_0 & -q_1 \\ q_3 & -q_2 & q_1 & q_0 \end{pmatrix},$$

$\mathbf{S}(\mathbf{q})$  being orthogonal,  $(\tau_x, \tau_y, \tau_z)^\top$  is the torque in the body-fixed frame, and  $I_{xx}, I_{yy}, I_{zz}$  are the diagonal elements of the moment of inertia tensor in the body-fixed frame (the off-diagonal elements being zero). The torque is given by the equation:

$$\tau^{(4)} = \frac{1}{2}\mathbf{S}^\top(\mathbf{q})\nabla_{\mathbf{q}}U(\mathbf{r}, \mathbf{q}) + \tau_{\text{int}}^{(4)}\tag{2.9}$$

where  $U$  is the potential energy and  $\tau_{\text{int}}^{(4)} = (\tau_{\text{int}}^{(0)}, 0, 0, 0)$  is the internal ‘torque’ which cancels any forces within the rigid body.

The Hamiltonian for a system of  $N$  rigid bodies, in quaternion representation, is:

$$H(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi}) = \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} + \sum_{i=1}^N \frac{1}{8}\boldsymbol{\pi}_i^\top \mathbf{S}(\mathbf{q}_i) \mathbf{I}^{-1} \mathbf{S}^\top(\mathbf{q}_i) \boldsymbol{\pi}_i + U(\mathbf{r}, \mathbf{q}),\tag{2.10}$$

where  $\mathbf{p}_i \in \mathbb{R}^3$  are the center-of-mass momenta conjugate to  $\mathbf{r}_i$  and  $\boldsymbol{\pi}_i \in \mathbb{R}^4$  are the angular momenta conjugate to  $\mathbf{q}_i$ .

### 2.3.3 A Numerical Integrator Scheme

The symplectic method derived by Miller et al. from the above equations [18] is based on re-writing the rotational kinetic energy term in Eq. (2.10) in the form

$$\frac{1}{8}\boldsymbol{\pi}^\top \mathbf{S}(\mathbf{q}) \mathbf{I}^{-1} \mathbf{S}^\top(\mathbf{q}) \boldsymbol{\pi} = \sum_{k=1}^3 V_k(\mathbf{q}, \boldsymbol{\pi}) = \sum_{k=1}^3 \frac{(\boldsymbol{\pi}^\top \mathbf{S}_k \mathbf{q})^2}{8I_k}, \quad (2.11)$$

where  $I_1 = I_{xx}$ ,  $I_2 = I_{yy}$ ,  $I_3 = I_{zz}$ , and the  $\mathbf{S}_k$  are permutation matrices defined as follows:

$$\begin{aligned} \mathbf{S}_1 \mathbf{q} &= (-q_1, q_0, q_3, -q_2)^\top, \\ \mathbf{S}_2 \mathbf{q} &= (-q_2, -q_3, q_0, q_1)^\top, \\ \mathbf{S}_3 \mathbf{q} &= (-q_3, q_2, -q_1, q_0)^\top. \end{aligned}$$

This allows the introduction of a second order integrator for free rotations  $(\mathbf{q}(t), \boldsymbol{\pi}(t)) = \mathcal{R}_t(\mathbf{q}(0), \boldsymbol{\pi}(0))$

$$\mathcal{R}^t = \mathcal{R}_1^{t/2} \circ \mathcal{R}_2^{t/2} \circ \mathcal{R}_3^t \circ \mathcal{R}_2^{t/2} \circ \mathcal{R}_1^{t/2},$$

where  $(\mathbf{q}', \boldsymbol{\pi}') = \mathcal{R}_k^t(\mathbf{q}, \boldsymbol{\pi})$  is defined as follows:

$$\begin{aligned} \mathbf{q}' &= \cos(\zeta_k t) \mathbf{q} + \sin(\zeta_k t) \mathbf{S}_k \mathbf{q}, \\ \boldsymbol{\pi}' &= \cos(\zeta_k t) \boldsymbol{\pi} + \sin(\zeta_k t) \mathbf{S}_k \boldsymbol{\pi}, \end{aligned}$$

with

$$\zeta_k = \frac{1}{4I_k} \boldsymbol{\pi}^\top \mathbf{S}_k \mathbf{q}.$$

This integrator, known as ‘NO\_SQUISH’, is symplectic, time reversible and exactly preserves the constraint  $|\mathbf{q}| = 1$ .

The resulting numerical scheme for microcanonical rigid body molecular dynamics is:

$$\begin{aligned}
\mathbf{p}_i^{n+\frac{1}{2}} &= \mathbf{p}_i^n + \frac{h}{2} \mathbf{f}_i^n, \\
\boldsymbol{\pi}_i^{n+\frac{1}{2}} &= \boldsymbol{\pi}_i^n + \frac{h}{2} \mathbf{F}_i^n, \\
\mathbf{r}_i^{n+1} &= \mathbf{r}_i^n + \frac{h}{m} \mathbf{p}_i^{n+\frac{1}{2}}, \\
(\mathbf{q}_i^{n+1}, \tilde{\boldsymbol{\pi}}_i^{n+\frac{1}{2}}) &= \mathcal{R}^h(\mathbf{q}_i^n, \boldsymbol{\pi}_i^{n+\frac{1}{2}}), \\
\boldsymbol{\pi}_i^{n+1} &= \tilde{\boldsymbol{\pi}}_i^{n+\frac{1}{2}} + \frac{h}{2} \mathbf{F}_i^{n+1}, \\
\mathbf{p}_i^{n+1} &= \mathbf{p}_i^{n+\frac{1}{2}} + \frac{h}{2} \mathbf{f}_i^{n+1},
\end{aligned}$$

where  $\mathbf{f}_i^n = -\partial U(\mathbf{r}^n, \mathbf{q}^n)/\partial \mathbf{r}_i$  is the translational force acting on the center of mass of molecule  $i$  and  $\mathbf{F}_i^n = -\partial U(\mathbf{r}^n, \mathbf{q}^n)/\partial \mathbf{q}_i$  is the rotational force which can be calculated from the torque acting on molecule  $i$ .

### 2.3.4 Smooth cutoff for rigid molecules

The approach outlined in Section 2.2.3 (page 9) is appropriate for single-site particles, but not for rigid body molecules with multiple coulombic interaction sites.

If the cutoff distance were based on the distance between individual interaction sites, then as two molecules approach the cutoff distance, some sites would be included in the computation, but not others. The effect would be artificially to introduce a net charge on the interacting bodies, whereas the simulated molecules themselves are neutral.

The Coulombic interaction potential between neutral bodies decays quite quickly. For neutral rigid bodies with a fixed electrical dipole moment (as is typical for rigid body molecular models), the decay is  $O(\frac{1}{r^3})$ , whereas the corresponding potential for bodies with an overall charge decays more slowly,  $O(\frac{1}{r})$ .

For this reason, basing the cutoff calculation on the distance between interaction sites, although the most natural and computationally straightforward, is not the best approach.

Instead, the cutoff distance is based on the centre-of-mass distance between the molecules. The general form of the interaction potential for a pair of molecules  $a$  and  $b$  now becomes:

$$U^{ab} = f(|\mathbf{r}_c^a - \mathbf{r}_c^b|) \sum_{i,j=1}^{n_{sites}} u_{ij}(|\mathbf{r}_i^a - \mathbf{r}_j^b|) \quad (2.12)$$

Here,  $u_{ij}$  is the interaction potential between site  $i$  of molecule  $a$  and site  $j$  of molecule  $b$ ,  $f$  is a smoothing function, for example that of Eq. (2.4),  $\mathbf{r}_i^a$  is the (space-fixed) position of site  $i$  of molecule  $a$ ,  $\mathbf{r}_c^a$  is the centre of mass of molecule  $a$ , and so on.

This potential is continuous, and so induces a conservative force field on the phase space. The derivation of the forces induced by this potential is straightforward, but we have been unable to find it in standard references on the subject (or any other publication), so it is included in detail below.

The total force on site  $k$  of molecule  $a$  due to molecule  $b$  is:

$$\mathbf{F}_k^{ab} = -\nabla_k^a U^{ab} = -\nabla_k^a \left\{ f(|\mathbf{r}_c^a - \mathbf{r}_c^b|) \sum_{i,j=1}^{n_{\text{sites}}} u_{ij}(|\mathbf{r}_i^a - \mathbf{r}_j^b|) \right\},$$

where  $\nabla_k^a$  is the vector operator whose three components are the partial derivatives with respect to the three spacial coordinates of site  $k$  of molecule  $a$ , and  $U^{ab}$  is the potential function of the spacial coordinates of molecules  $a$  and  $b$ .

Writing  $\mathbf{r}_c = \mathbf{r}_c^a - \mathbf{r}_c^b$ , and expanding the above derivative gives:

$$\mathbf{F}_k^{ab} = -f(|\mathbf{r}_c|) \sum_{j=1}^{n_{\text{sites}}} \nabla_k^a u_{kj}(|\mathbf{r}_k^a - \mathbf{r}_j^b|) - \{\nabla_k^a f(|\mathbf{r}_c|)\} \sum_{i,j=1}^{n_{\text{sites}}} u_{ij}(|\mathbf{r}_i^a - \mathbf{r}_j^b|).$$

Now writing  $m_k$  for the mass of site  $k$  of molecule  $a$ , and  $M$  for that molecule's total mass, the second half of the above sum becomes:

$$\{\nabla_k^a f(|\mathbf{r}_c|)\} \sum_{i,j=1}^{n_{\text{sites}}} u_{ij}(|\mathbf{r}_i^a - \mathbf{r}_j^b|) = \frac{m_k}{M} f'(|\mathbf{r}_c|) \hat{\mathbf{r}}_c \sum_{i,j=1}^{n_{\text{sites}}} u_{ij}(|\mathbf{r}_i^a - \mathbf{r}_j^b|),$$

where  $\hat{\mathbf{r}}_c$  is the unit vector in the direction of  $\mathbf{r}_c$ . So the force can now be written as:

$$\mathbf{F}_k^{ab} = -f(|\mathbf{r}_c|) \sum_{j=1}^{n_{\text{sites}}} \nabla_k^a u_{kj}(|\mathbf{r}_k^a - \mathbf{r}_j^b|) - \frac{m_k}{M} f'(|\mathbf{r}_c|) \hat{\mathbf{r}}_c \sum_{i,j=1}^{n_{\text{sites}}} u_{ij}(|\mathbf{r}_i^a - \mathbf{r}_j^b|).$$

Finally, introducing the definitions:

$$\mathbf{F}_{uncut} = -\nabla_k^a u_{kj}(|\mathbf{r}_k^a - \mathbf{r}_j^b|) \text{ and}$$

$$\mathbf{F}_{cut} = -f'(|\mathbf{r}_c|)\hat{\mathbf{r}}_c \sum_{i=1}^{n_{sites}} u_{ij}(|\mathbf{r}_i^a - \mathbf{r}_j^b|),$$

we can express the force as the sum of two vectors:

$$\mathbf{F}_k^{ab} = f(|\mathbf{r}_c|)\mathbf{F}_{uncut} + \frac{m_k}{M}\mathbf{F}_{cut}. \quad (2.13)$$

The first vector corresponds to the force without cutoff, but scaled down within the cutoff band. The second vector is a ‘cutoff correction’ – its direction is always the line joining the molecular centres of mass.

The correction component only appears within the cutoff band. So centering the cutoff at the mass-centre of each molecule has a non-physical side-effect: site interaction forces no longer act in the direction joining the two sites – they veer towards alignment with the line joining the centres-of-mass as the molecules approach cutoff distance.

Note that  $\mathbf{F}_{cut}$  is independent of the site  $k$  – it can be calculated once, and used for all the sites of molecule  $a$ . Also, within the cutoff band, the interaction force between two sites involves the (uncut) potential between *all* the site interactions for the molecule pair. The forces calculation routine therefore needs to be re-organised to calculate all uncut potentials before calculating any cutoff forces. The following pseudo-code shows how to achieve this:

```

for all neighbour list molecule pairs  $(M^a, M^b)$  do
   $r_c$  = centre-of-mass distance between molecule pairs;
  if  $r_c < r_{cut}$  then
     $U^{ab} = 0$  (initialise inter-molecular potential);
    for  $S_i^a \in \{\text{sites of } M^a\}$  do
      for  $S_j^b \in \{\text{sites of } M^b\}$  do
        calculate (uncut) interaction potential  $u(S_i^a, S_j^b)$ ;
        calculate (uncut) interaction force  $\mathbf{f}(S_i^a, S_j^b)$ ;
         $U^{ab} = U^{ab} + u(S_i^a, S_j^b)$ ;
      end
    end
    if  $r_c > r_{mod}$  then
      Adjust  $\mathbf{f}(:, :)$  according to Eq. (2.13), using  $U^{ab}$ ;
      Adjust  $U^{ab}$  according to Eq. (2.12);
    end
    perform the standard torque and force calculations for all sites;
  end
end

```

**Algorithm 1:** Smooth potential cutoff for rigid molecules

## 2.4 Free Energy Calculation

A nonequilibrium work method was chosen to calculate the free energy for this work. Earlier studies to calculate free energy by simulation have often used the technique of thermodynamic integration. Both methods are valid for free energy calculation. There follows an explanation of the nonequilibrium method employed here, a comparison with thermodynamic integration, and some justification for the decision to use a nonequilibrium method.

Each step of the procedure outlined in Section 4.2 (page 45) is a transformation of the system from one state to another. The free energy between these states can be written as [19, Section 7.1.6]:

$$\Delta F = \int_0^1 \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda, \quad (2.14)$$

where  $\langle \cdots \rangle_\lambda$  denotes an equilibrium ensemble average for a system with potential energy  $U(\lambda)$ , and  $\lambda$  is a coupling parameter which drives the system between the two states. The technique of thermodynamic integration approximates the above integral by estimating the integrand for a discrete set of values of  $\lambda$ . For each such value, the system is equilibrated, then run for sufficient time for a reasonable estimate of the average potential gradient to be calculated. A simple quadrature then provides an estimate of the free energy.

To calculate the free energy between two states using the nonequilibrium approach [20], a number of trajectories are run. The starting point for each forward trajectory is chosen at random from the *equilibrated* starting state. A molecular dynamics run is then performed, starting from this point, during which the system is smoothly driven to the ending state, creating a single forward trajectory between the two states. Reverse trajectories are similar – they start from a randomly chosen point in the equilibrated ending state, and are driven smoothly to the starting state. As they run, the trajectories are not in equilibrium. The precise value of the free energy is calculated based on an ensemble average over all such trajectories [21]. As many trajectories are run as necessary to provide good sampling.

In practice, random starting points for the trajectories are generated as follows. A molecular dynamics equilibration run is performed in the starting state. After the system has reached equilibrium, the run continues, and a snapshot of the system is saved at regular intervals of time. Providing this time interval is sufficiently large, adjacent snapshots have negligible correlation, and the snapshots will represent a random sample of independent states.

To drive the system between states, its potential,  $U$ , is modified via a coupling parameter  $\lambda(t)$ , which transforms the system from its initial state,  $\lambda(0)$ , to its final state,  $\lambda(T)$ . For a particular trajectory, the (non-equilibrium) work done is then computed [19, Section 7.4.1] as:

$$W = \int_{t=0}^T \frac{\partial U(\Gamma(t); \lambda)}{\partial \lambda} \dot{\lambda}(t) dt, \quad (2.15)$$

where  $\Gamma(t)$  is the path in phase space of the trajectory. The speed of the coupling parameter  $\dot{\lambda} = d\lambda/dt$  can be time dependent,  $\dot{\lambda}(t)$ , and tailored to slow the trajectory over regions where relaxation time of the system to equilibrium is relatively slow, and therefore subject to hysteresis. This ability to vary the trajectory speed is a useful device for concentrating computing time on the problematic regions of the

state transition. For this work, this was achieved with a set of discrete jumps, that is, trajectory speed is a piecewise constant function of time. This approach proved adequate, though it would also be possible to use more complex functions to vary the speed smoothly. The only requirement imposed in the derivation of Eq. 2.16 is that the reverse path matches the forward path, that is  $\lambda_f(t) = \lambda_r(T - t)$ , where  $\lambda_f$  is the forward path,  $\lambda_r$  is the reverse path, and  $T$  is the total trajectory time.

The measurements of nonequilibrium work in both forward and reverse directions are used to determine the free energy difference between the initial and final states,  $\Delta F$ , according to the Bennett Acceptance Ratio (BAR) equation:

$$\sum_{i=1}^{n_F} \frac{1}{1 + e^{\beta(M+W_i-\Delta F)}} = \sum_{j=1}^{n_R} \frac{1}{1 + e^{-\beta(M+W_j-\Delta F)}} , \quad (2.16)$$

where  $\beta = 1/k_B T$ ,  $M = k_B T \ln(n_F/n_R)$ , and  $n_F$  ( $n_R$ ) is the number of forward (reverse) trajectories. This equation, originally derived by Bennett [22] for the case of instantaneous switching between two equilibrium states, has been shown [20] to be also valid when the potential energy difference between the two states is replaced with the nonequilibrium work values for finite time switching processes in the forward and reverse directions.

As an estimator for the free energy, this equation is optimal in the statistical sense of a Maximum Likelihood Estimator [23]. The variance in the obtained value for the free energy can be estimated as follows [21]:

$$\sigma_{\text{BAR}}^2 = \frac{1}{\beta^2 n_{\text{tot}}} \left\{ \left\langle \frac{1}{2 + 2\cosh(\beta(M + W_i - \Delta F))} \right\rangle^{-1} \left( \frac{n_{\text{tot}}}{n_F} + \frac{n_{\text{tot}}}{n_R} \right) \right\} , \quad (2.17)$$

where  $n_{\text{tot}} = n_F + n_R$  and the average, denoted by the angle brackets, is over all work measurements, both forward and reverse.

Nonequilibrium methods, in various forms, have been in use for several decades. They provide comparable accuracy to thermodynamic integration (for given computing resources). In addition, they offer some important advantages:

**Hysteresis detection:** Since forward and reverse trajectories are combined in the BAR calculation, any hysteresis will show up as a significant difference between forward and reverse work, which in turn will be reflected in a high error estimate. So the method itself contains a built-in check for hysteresis.

**Few equilibration runs:** Within the nonequilibrium approach it is only necessary to equilibrate the system at the initial and final states. Such states are usually far from any thermodynamic transition points and thus the equilibration is rapid. To use thermodynamic integration, it is necessary to equilibrate the system at many intermediate states. States that are close to thermodynamic transition points may exhibit weak ergodicity and thus require very long equilibration runs.

**Additional trajectories can improve accuracy:** If additional accuracy is required, further trajectories can be run after the initial results have been collected. The results are added to the results of the earlier trajectories, so improved accuracy can be obtained without discarding the earlier computations.

**Trajectories can be run in parallel:** The free energy is calculated as an average from a number of independent trajectories. Being independent, these trajectories can be run simultaneously on separate processors, without the computational overhead of processor messaging and co-ordination inherent in, for example, MPI software.

An appropriate speed for the trajectories must be established: good accuracy can only be achieved with a slow enough trajectory speed so that the system is never driven far from equilibrium, and the forward and reverse work distributions overlap somewhat.

### 2.4.1 Exponential Averaging

The BAR equation, Eq. 2.16, requires a set of trajectories in both directions. It is also possible, though with less certainty as to the accuracy, to estimate the free energy from a set of trajectories in one direction only using the exponential average:

$$\Delta F \approx \frac{\log \left( \frac{\sum_{i=1}^N e^{-\beta W_i}}{N} \right)}{\beta}, \text{ where } \beta = \frac{1}{k_B T}. \quad (2.18)$$

Jarzynski showed [21] that this estimate tends to the true free energy in the limit of large  $N$ .

## 2.5 Thermostats

### 2.5.1 The Need for a Thermostat

Using a molecular dynamics simulation to solve the equations of motion for any isolated system will result in a microcanonical (constant energy) simulation. For the cleaving method to be successful, the path needs to be reversible, which requires that the ice–water system be maintained at co-existence conditions throughout the simulation. To maintain the ice and water at the melting point, the temperature and pressure must remain constant. For this reason, the microcanonical ensemble is not appropriate. In fact, when using the cleaving method, the system is not isolated: an external potential influences the system at each step in order to form the interface. A side-effect of these external potentials is to cause even more temperature drift than would be the case for an isolated system. A method of controlling the temperature is therefore essential.

Temperature is controlled by means of a thermostat. A thermostat is a modification to the equations of motion designed to model a heat bath. If the system temperature starts to drift, the heat bath will interact with it to keep the average temperature constant, so that the system corresponds to the ‘canonical’ thermodynamic ensemble.

The approach for controlling the temperature for this work evolved as we gained more experience with the water models.

The first model to be studied was TIP4P with discontinuous truncation of all interactions at 10Å (Chapter 5, page 66). For this model, temperature was controlled using the Nosé-Hoover method, summarised in Section 2.5.3 (page 23).

After this, we studied two models (TIP4P and TIP4P-Ew) using Ewald Sums for long-range forces (Chapter 6, page 71). For this model, temperature was controlled using a newly-developed rigid-body Langevin thermostat, summarised in Section 2.5.5 (page 27).

### 2.5.2 Thermostats for Rigid Body Systems

There is no unique definition of temperature; it can be measured in many ways. In general, different measurements of temperature will give different results, unless the system is in equilibrium. In the case of an equilibrium system, the temperature is well-defined, that is, the temperature is independent of the method used to measure

it. Since free energy is a property of equilibrium systems, and our simulations need to stay close to equilibrium to give accurate estimates of this property, our simulations must be designed to keep the system as close to equilibrium as possible. It would be possible to use a thermostat which influenced only the translational motion of the molecules; such a thermostat would control the ‘translational’ measure of temperature. Once the ‘translational’ temperature has shifted due to the influence of the thermostat, the system is out of equilibrium until the rotational motions ‘catch up’, which they will do in time, due to the natural tendency of the system to settle to equilibrium. However, equilibrium is maintained indirectly, relying on the coupling between translational and rotational motions to restore equilibrium *after* the influence of the thermostat on the translational motions. The speed of this coupling depends on the mechanics of the molecules, that is, their geometry and weight distribution. It seems reasonable to conclude that a thermostat which influences more degrees of freedom, and therefore relies less on the natural coupling between degrees of freedom, will result in a system which stays closer to equilibrium. In the case of Langevin thermostats, our empirical trials with different thermostats confirm this conclusion, as detailed in Section 2.5.5 (page 27), where we show that an ‘optimal’ (in a sense made precise in the discussion) thermostat is one which influences all degrees of freedom with roughly the same ‘strength’. Of course, no thermostat is perfect, they all disturb equilibrium; what we have shown is that if a thermostat spreads its disturbances over more degrees of freedom, then the recovery time from these disturbances to equilibrium is faster, in other words, the system is kept closer to equilibrium.

All of the simulations in this work therefore utilise thermostats with direct influence over both translational and rotational motion of the rigid body molecules.

### 2.5.3 The Nosé-Hoover Thermostat

Throughout the 1970s and early 1980s, temperature control was achieved by ad-hoc periodical scaling of all the molecular velocities [24]. This method is simple to implement, and in practice it seems to give reasonable results in many situations, but it has no theoretical justification, the underlying system can not be shown to be Hamiltonian, or to generate a canonical (or any other) thermodynamic distribution.

In 1984, Nosé devised the following Hamiltonian:

$$H_{\text{Nosé}} = U(\mathbf{r}) + \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m_i s^2} + (g+1)k_B T \ln s + p_s^2/2Q, \quad (2.19)$$

in which two new conjugate variables  $s$  and  $p_s$  have been added to the original Hamiltonian system with  $g$  degrees of freedom. Nosé showed that the evolution is canonical, that is, the new variables (which can be regarded as ‘time-scaling’) correspond to a heat bath in contact with the original system. The constant  $Q$  represents the strength of coupling between heat bath and system.

Shortly after Nosé published this result, William Hoover showed [25] that the equations of motion resulting from Nosé’s Hamiltonian can be re-formulated in a simpler form, without the time-scaling variable, as follows:

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i}, \\ \dot{\mathbf{p}}_i &= -\frac{\partial U(\mathbf{r})}{\partial \mathbf{r}_i} - \mathbf{p}_i \frac{p_\eta}{Q}, \\ \dot{p}_\eta &= \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{m_i} - Nk_B T, \\ \dot{\eta} &= \frac{p_\eta}{Q}, \end{aligned}$$

where  $\eta$  and  $p_\eta$  are new conjugate variables, and, as before,  $Q$  determines the ‘coefficient of friction’, or the strength with which the thermostat interacts with the system. Hoover showed that the above equations of motion generate a canonical distribution about the temperature corresponding to  $k_B T$ .

Note that  $\eta$  does not appear in the equations for other variables, and does not need to be included in a numerical solution of the system dynamics. However we included its calculation in all our simulations in order to monitor the ‘extended energy’ of the system, which is a conserved quantity of the Nosé-Hoover equations of motion:

$$E_{\text{ext}} = U(\mathbf{r}) + \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m_i s^2} + \frac{p_\eta^2}{2Q} + gk_B T \eta. \quad (2.20)$$

Recording the value of  $E_{\text{ext}}$  periodically during simulations provides a useful check – if the value does not remain constant (within numerical error), this indicates an error in the implementation of the algorithm.

Nosé's equations, in the simplified form discovered by Hoover, rapidly gained favour with the molecular simulation community, and became known as the 'Nosé-Hoover' thermostat. Incidentally, it was Nosé's results which motivated Hoover to develop his equations, but, unlike Nosé, he did not know the Hamiltonian which gives rise to them; that was not discovered for another twelve years [24].

The symplectic quaternion-based scheme for rigid body motion, described in Section 2.3.3 (page 14), can be modified to incorporate two Nosé-Hoover thermostats, one for translational, and a second for rotational motion. For the translational thermostat, we replace  $Q$ , with  $Q_{\text{tra}}$ , and  $p_\eta$  with  $s/Q_{\text{tra}}$ , and for the rotational thermostat, we replace  $Q$  with  $Q_{\text{rot}}$ ,  $\eta$  with  $\nu$ , and  $p_\eta$  with  $\sigma/Q_{\text{rot}}$ . The resulting numerical scheme for canonical rigid body molecular dynamics is:

$$\begin{aligned}
\mathbf{p}_i^{n+\frac{1}{2}} &= \frac{(\mathbf{p}_i^n + \frac{h}{2}\mathbf{f}_i^n)}{(1 + \frac{h}{2}s^n)}, \\
\boldsymbol{\pi}_i^{n+\frac{1}{2}} &= \frac{(\boldsymbol{\pi}_i^n + \frac{h}{2}\mathbf{F}_i^n)}{(1 + \frac{h}{2}\sigma^n)}, \\
\mathbf{r}_i^{n+1} &= \mathbf{r}_i^n + \frac{h}{m}\mathbf{p}_i^{n+\frac{1}{2}}, \\
(\mathbf{q}_i^{n+1}, \tilde{\boldsymbol{\pi}}_i^{n+\frac{1}{2}}) &= \mathcal{R}^h(\mathbf{q}_i^n, \boldsymbol{\pi}_i^{n+\frac{1}{2}}), \\
s^{n+1} &= s^n + \frac{h\phi_{\text{tra}}(\mathbf{p}^{n+\frac{1}{2}})}{Q_{\text{tra}}}, \\
\sigma^{n+1} &= \sigma^n + \frac{h\phi_{\text{rot}}(\mathbf{q}^{n+1}, \tilde{\boldsymbol{\pi}}^{n+\frac{1}{2}})}{Q_{\text{rot}}}, \\
\eta^{n+1} &= \eta^n + \frac{h}{2}(s^n + s^{n+1}), \\
\nu^{n+1} &= \nu^n + \frac{h}{2}(\sigma^n + \sigma^{n+1}), \\
\mathbf{p}_i^{n+1} &= \mathbf{p}_i^{n+\frac{1}{2}}(1 - \frac{h}{2}s^{n+1}) + \frac{h}{2}\mathbf{f}_i^{n+1}, \\
\boldsymbol{\pi}_i^{n+1} &= \tilde{\boldsymbol{\pi}}_i^{n+\frac{1}{2}}(1 - \frac{h}{2}\sigma^{n+1}) + \frac{h}{2}\mathbf{F}_i^{n+1}.
\end{aligned} \tag{2.21}$$

Here

$$\begin{aligned}
\phi_{\text{tra}}(\mathbf{p}) &= \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{m} - g_{\text{tra}}k_B T, \\
\phi_{\text{rot}}(\mathbf{q}, \boldsymbol{\pi}) &= 2 \sum_{i=1}^N \sum_{j=1}^3 V_j(\mathbf{q}_i, \boldsymbol{\pi}_i) - g_{\text{rot}}k_B T,
\end{aligned}$$

where  $g_{\text{tra}} = 3N - 3$  is the number of translational degrees of freedom (taking into account the constraints of the total momentum conservation), and  $g_{\text{rot}} = 3N$  is the number of rotational degrees of freedom. We use the fact that  $\phi_{\text{rot}} \circ \mathcal{R}^t = \phi_{\text{rot}}$  and so  $\phi_{\text{rot}}(\mathbf{q}^{n+1}, \tilde{\boldsymbol{\pi}}^{n+\frac{1}{2}}) = \phi_{\text{rot}}(\mathbf{q}^n, \boldsymbol{\pi}^{n+\frac{1}{2}})$ . The initial conditions for the thermostat variables are  $s^0 = \sigma^0 = \eta^0 = \nu^0 = 0$ . As noted above, the thermostat variables  $\eta$  and  $\nu$  are integrated only for the purposes of checking that the extended energy,

$$E_{\text{ext}} = U(\mathbf{r}) + \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m_i s^2} + \frac{1}{2} Q_{\text{tra}} s^2 + g_{\text{tra}} k_B T \eta + \frac{1}{2} Q_{\text{rot}} \sigma^2 + g_{\text{rot}} k_B T \nu, \quad (2.22)$$

is conserved.

To modify this algorithm for the control of only translational (rotational) kinetic temperature, set  $\sigma^{n+1} = \sigma^n = 0$  ( $s^{n+1} = s^n = 0$ ), which is equivalent to setting  $Q_{\text{rot}}^{-1} = 0$  ( $Q_{\text{tra}}^{-1} = 0$ ). It is also possible to modify the algorithm so that both temperatures are controlled by a single thermostat. To achieve this, set  $\sigma^n = s^n$  and replace  $\phi_{\text{tra}}(\mathbf{p})$  with

$$\phi(\mathbf{p}, \mathbf{q}, \boldsymbol{\pi}) = \phi_{\text{tra}}(\mathbf{p}) + \phi_{\text{rot}}(\mathbf{q}, \boldsymbol{\pi})$$

and  $Q_{\text{tra}}$  with a single thermostat weight parameter  $Q$ .

### 2.5.4 Nosé-Hoover and the Cleaving Method

As described in Section 2.5.3 (page 23), there is more than one way of adapting the Nosé-Hoover algorithm to influence rotational as well translation motions in a rigid-body dynamics simulation. We chose to use two independent thermostats to control the two kinds of motion, the scheme illustrated in Eqs. 2.21.

Since the Cleaving Method starts with two isolated systems, two separate thermostats (more precisely, two separate pairs of thermostats) were used for the two isolated systems. This now raises a question in step 3 (see Section 4.7, page 56), where the systems are merged together; at the start of the merge, there are two isolated systems, and at the end a single system. In transition, it is neither one thing nor the other, so it is not clear how many thermostats are appropriate during the step 3 transition.

Our first approach was to use a single thermostat (pair) for the combined system from the start of step 3. However, this approach proved unsatisfactory, since at the

beginning of step 3, the two systems are still isolated. A Nosé-Hoover thermostat adds a single degree of freedom to the system, which is coupled in the same way to each molecule, and so relies on coupling within the system to disperse the heat evenly. The isolation of the two systems at the starting point of step 3 resulted in a heat transfer between the ice and water systems during equilibration, and thus caused a discontinuity in the trajectory path. We therefore abandoned this approach, and instead, used two separate thermostat pairs throughout step 3, until the transformation to a single system was complete. Then a single thermostat pair was used from the start of step 4. This was the approach which was settled on for the truncated system (Chapter 5, page 66).

However, further experimental runs revealed that this approach is also unsatisfactory. When switching to Ewald Sums, it became all the more important to minimise the overall simulation time required to merge the systems. One way of helping with this is to postpone the cooling down of the water system to step 4 (this point is discussed in detail in Section 4.7, page 56). With the water molecules at 70% strength, and the ice molecules at full strength, a severe discontinuity was observed when switching from 2 thermostat pairs to 1 thermostat pair at the start of step 4. Further experimental runs revealed that this discontinuity is still present (though far less severe) with the water molecules at full strength. The effect was also more pronounced when using a discontinuous cutoff. The effect is probably related to the inhomogeneity (half-ice, half-water) of the combined system.

Another possible approach (which we have not explored) would be to retain two separate thermostat pairs throughout the transformation – this would certainly make the path continuous, but in light of the observation that the system equilibrium is altered slightly when changing the number of thermostats, the validity would still be questionable. We conclude that the Nosé-Hoover method presents some difficulties when applied to the merging of two systems into one, and an alternative type of thermostat would be preferable.

### 2.5.5 The Langevin Thermostat

The Langevin thermostat differs from the Nosé-Hoover thermostat in that it is non-deterministic, and it acts independently on each degree of freedom in the system. Since this type of thermostat acts independently on each molecule, it does not suffer

from the shortcomings described above, and is therefore a better choice for use with the cleaving method.

However, as discussed in Section 2.5.2 (page 22), we would like the thermostat to influence all degrees of freedom, rather than, for example, influencing only translational motions and relying on efficient heat flow between translational and rotational motions for the rotational motions to ‘catch up’. Although Langevin methods to control the translational motion are well established, there was (at the time we started this work) no such method to control all the degrees of freedom in the rigid-body dynamics context. Since such a method would be of use in this context (and is also a mathematical problem of intrinsic interest), we decided, in collaboration with Professor Michael Tretyakov of Leicester University, a specialist in stochastic processes, to work on its development. This work resulted in several Langevin-type methods for quaternion rigid-body dynamics. We published these results separately [26], in a paper which covered both the mathematical development and a detailed experimental analysis using TIP4P water. Here we give details of the particular method used in this work; a more comprehensive treatment is provided in the separate publication.

Combining equations 2.10 and 2.11 gives the following form of the Hamiltonian:

$$H(\mathbf{r}, \mathbf{p}, \mathbf{q}, \boldsymbol{\pi}) = \frac{\mathbf{p}^\top \mathbf{p}}{2m} + \sum_{j=1}^n \sum_{k=1}^3 V_k(\mathbf{q}_j, \boldsymbol{\pi}_j) + U(\mathbf{r}, \mathbf{q}). \quad (2.23)$$

The Hamilton equations of motion, in terms of the  $\mathbf{r}$ ,  $\mathbf{q}$  and their conjugates  $\mathbf{p}$  and  $\boldsymbol{\pi}$  are:

$$\begin{aligned} \frac{d\mathbf{r}}{dt} &= \frac{\mathbf{p}}{m}, \\ \frac{d\mathbf{p}}{dt} &= -\nabla_{\mathbf{r}} U(\mathbf{r}, \mathbf{q}), \\ \frac{d\mathbf{q}_j}{dt} &= \sum_{l=1}^3 \nabla_{\boldsymbol{\pi}_j} V_l(\mathbf{q}_j, \boldsymbol{\pi}_j), \\ \frac{d\boldsymbol{\pi}_j}{dt} &= -\sum_{l=1}^3 \nabla_{\mathbf{q}_j} V_l(\mathbf{q}_j, \boldsymbol{\pi}_j) - \nabla_{\mathbf{q}_j} U(\mathbf{r}, \mathbf{q}), \quad j = 1, \dots, n. \end{aligned} \quad (2.24)$$

It is easy to check that if the initial conditions are chosen such that  $|\mathbf{q}_j(0)| = 1$ , then the corresponding Hamilton equations of motion ensure that

$$|\mathbf{q}_j(t)| = 1, \quad j = 1, \dots, n, \quad \text{for all } t \geq 0. \quad (2.25)$$

We derive a stochastic thermostat for this molecular system, which preserves (2.25), from the Langevin-type equations (in the form of Ito):

$$dR^j = \frac{P^j}{m} dt, \quad R^j(0) = r^j, \quad (2.26)$$

$$dP^j = -\nabla_{r^j} U(\mathbf{R}, \mathbf{Q}) dt - \gamma g(P^j, R^j) dt + b(R^j) dw^j(t), \quad P^j(0) = p^j,$$

$$dQ^j = \sum_{l=1}^3 \nabla_{\pi^j} V_l(Q^j, \Pi^j) dt, \quad Q^j(0) = q^j, \quad |q^j| = 1,$$

$$d\Pi^j = -\sum_{l=1}^3 \nabla_{q^j} V_l(Q^j, \Pi^j) dt - \nabla_{q^j} U(\mathbf{R}, \mathbf{Q}) dt \quad (2.27)$$

$$-\Gamma G(Q^j, \Pi^j) dt + B(Q^j, \Pi^j) dW^j(t), \quad \Pi^j(0) = \pi^j,$$

$$j = 1, \dots, n,$$

where  $\gamma > 0$  and  $\Gamma \geq 0$  are the friction coefficients for the translational and rotational motions, respectively, measured in units of inverse time, which control the strength of coupling of the system to the ‘heat bath’;  $g$  is a 3-dimensional appropriately normalized vector;  $G$  is a 4-dimensional vector, which provides an appropriate balance in coupling various rotational degrees of freedom with the ‘heat bath’;  $b$  and  $B$  are 3-by-3 and 4-by-4 matrices, respectively; and  $(\mathbf{w}^\top, \mathbf{W}^\top)^\top = (w^1{}^\top, \dots, w^n{}^\top, W^1{}^\top, \dots, W^n{}^\top)^\top$  is a  $(3n + 4n)$ -dimensional standard Wiener process with  $w^j = (w_1^j, w_2^j, w_3^j)^\top$  and  $W^j = (W_0^j, W_1^j, W_2^j, W_3^j)^\top$ .

The resulting ‘*Langevin thermostat*’ (see [26] for the full derivation) is the following stochastic system:

$$G(q, \pi) = J(q)\pi \quad \text{and} \quad B_{ii}^2 = \frac{2M\Gamma}{\beta}$$

$$J(q) = \frac{\sum_{l=1}^3 \frac{1}{I_l} S_l q [S_l q]^\top}{\sum_{k=1}^3 \frac{1}{I_k}} \quad \text{and} \quad M = \frac{4}{\sum_{l=1}^3 \frac{1}{I_l}}. \quad (2.28)$$

$$dR^j = \frac{P^j}{m}dt, \quad R^j(0) = r^j, \quad (2.29)$$

$$dP^j = -\nabla_{r^j}U(\mathbf{R}, \mathbf{Q})dt - \gamma P^j dt + \sqrt{2m\gamma/\beta}dw^j(t), \quad P^j(0) = p^j,$$

$$dQ^j = \sum_{l=1}^3 \nabla_{\pi^j} V_l(Q^j, \Pi^j)dt, \quad Q^j(0) = q^j, \quad |q^j| = 1,$$

$$d\Pi^j = -\sum_{l=1}^3 \nabla_{q^j} V_l(Q^j, \Pi^j)dt - \nabla_{q^j}U(\mathbf{R}, \mathbf{Q})dt \quad (2.30)$$

$$-\Gamma J(Q^j)\Pi^j dt + \sqrt{2M\Gamma/\beta}dW^j(t), \quad \Pi^j(0) = \pi^j,$$

$$j = 1, \dots, n,$$

where the notation is as in (2.26)-(2.27).

The integrator is based on splitting the Langevin system (2.29)-(2.30) into the Hamiltonian system with additive noise (i.e. (2.29)-(2.30) without the damping terms) and the deterministic system of linear differential equations of the form

$$\dot{\mathbf{p}} = -\gamma \mathbf{p} \quad (2.31)$$

$$\dot{\boldsymbol{\pi}}^j = -\Gamma J(\mathbf{q}^j)\boldsymbol{\pi}^j, \quad j = 1, \dots, n.$$

We construct a second-order weak quasi-symplectic integrator for the stochastic Hamiltonian system [27, 28] and appropriately concatenate it [29, 28] with the exact solution of (2.31). The resulting numerical method is given below. We assume that the system (2.29)-(2.30) has to be solved on a time interval  $[0, T]$  and for simplicity we use uniform time discretization with the step  $h = T/N$ . Introduce the diagonal  $4 \times 4$  matrix  $D$

$$Dq := \frac{2M\Gamma}{\beta} \sum_{i=0}^3 \frac{\partial^2}{\partial \pi_i^2} \sum_{l=1}^3 \nabla_q V_l(q, \pi) = \frac{M\Gamma}{\beta} \begin{bmatrix} q_0 \left( \frac{1}{I_1} + \frac{1}{I_2} + \frac{1}{I_3} \right) \\ q_1 \left( \frac{1}{I_1} + \frac{1}{I_2} + \frac{1}{I_3} \right) \\ q_2 \left( \frac{1}{I_1} + \frac{1}{I_2} + \frac{1}{I_3} \right) \\ q_3 \left( \frac{1}{I_1} + \frac{1}{I_2} + \frac{1}{I_3} \right) \end{bmatrix} \quad (2.32)$$

and the mapping  $\Psi_l(t; q, \pi) = (\mathcal{Q}, \Pi)$  defined by

$$\begin{aligned}\mathcal{Q} &= \cos\left(t\frac{1}{4I_l}\pi^\top S_l q\right) q + \sin\left(t\frac{1}{4I_l}\pi^\top S_l q\right) S_l q, \\ \Pi &= \cos\left(t\frac{1}{4I_l}\pi^\top S_l q\right) \pi + \sin\left(t\frac{1}{4I_l}\pi^\top S_l q\right) S_l \pi.\end{aligned}\quad (2.33)$$

The *quasi-symplectic scheme* for (2.29)-(2.30) can be written in the form

$$\begin{aligned}\mathbf{P}_0 &= \mathbf{p}, \quad \mathbf{R}_0 = \mathbf{r}, \quad \mathbf{Q}_0 = \mathbf{q}, \quad \Pi_0 = \pi, \\ \mathcal{P}_{1,k} &= \mathbf{P}_k \exp(-\gamma h/2), \quad \Pi_{1,k}^j = \Pi_k^j \exp(-\Gamma J(Q_k^j)h/2), \quad j = 1, \dots, n, \\ \mathcal{P}_{2,k} &= \mathcal{P}_{1,k} - \frac{h}{2} \nabla_{\mathbf{r}} U(\mathbf{R}_k, \mathbf{Q}_k) + \frac{h^{1/2}}{2} \sqrt{2m\gamma/\beta\xi_k} \\ \Pi_{2,k}^j &= \Pi_{1,k}^j - \frac{h}{2} \nabla_{q^j} U(\mathbf{R}_k, \mathbf{Q}_k) + \frac{h^{1/2}}{2} \sqrt{2M\Gamma/\beta\eta_k^j} - \frac{h^2}{16} DQ_k^j, \quad j = 1, \dots, n, \\ \mathbf{R}_{k+1} &= \mathbf{R}_k + \frac{h}{m} \mathcal{P}_{2,k},\end{aligned}\quad (2.34)$$

$$\begin{aligned}(\mathcal{Q}_{1,k}^j, \Pi_{3,k}^j) &= \Psi_3(h/2; Q_k^j, \Pi_{2,k}^j) \\ (\mathcal{Q}_{2,k}^j, \Pi_{4,k}^j) &= \Psi_2(h/2; \mathcal{Q}_{1,k}^j, \Pi_{3,k}^j) \\ (\mathcal{Q}_{3,k}^j, \Pi_{5,k}^j) &= \Psi_1(h; \mathcal{Q}_{2,k}^j, \Pi_{4,k}^j) \\ (\mathcal{Q}_{4,k}^j, \Pi_{6,k}^j) &= \Psi_2(h/2; \mathcal{Q}_{3,k}^j, \Pi_{5,k}^j) \\ (\mathcal{Q}_{k+1}^j, \Pi_{7,k}^j) &= \Psi_3(h/2; \mathcal{Q}_{4,k}^j, \Pi_{6,k}^j), \quad j = 1, \dots, n,\end{aligned}$$

$$\begin{aligned}\Pi_{8,k}^j &= \Pi_{7,k}^j - \frac{h}{2} \nabla_{q^j} U(\mathbf{R}_{k+1}, \mathbf{Q}_{k+1}) + \frac{h^{1/2}}{2} \sqrt{2M\Gamma/\beta\eta_k^j} - \frac{h^2}{16} DQ_{k+1}^j, \quad j = 1, \dots, n, \\ \mathcal{P}_{3,k} &= \mathcal{P}_{2,k} - \frac{h}{2} \nabla_{\mathbf{r}} U(\mathbf{R}_{k+1}, \mathbf{Q}_{k+1}) + \frac{h^{1/2}}{2} \sqrt{2m\gamma/\beta\xi_k},\end{aligned}$$

$$\begin{aligned}\mathbf{P}_{k+1} &= \mathcal{P}_{3,k} \exp(-\gamma h/2), \quad \Pi_{k+1}^j = \Pi_{8,k}^j \exp(-\Gamma J(Q_{k+1}^j)h/2), \quad j = 1, \dots, n, \\ k &= 0, \dots, N-1,\end{aligned}$$

where  $\xi_k = (\xi_{1,k}, \dots, \xi_{3n,k})^\top$  and  $\eta_k^j = (\eta_{1,k}^j, \dots, \eta_{4,k}^j)^\top$ ,  $j = 1, \dots, n$ , with their components being i.i.d. with the same law

$$P(\theta = 0) = 2/3, \quad P(\theta = \pm\sqrt{3}) = 1/6. \quad (2.35)$$

The scheme 2.34 can be shown to be a quasi-symplectic, second-order method.

We performed a set of experiments to investigate the performance of the thermostat under a range of possible weights. Performance is measured by running the following experiment:

- Equilibrate a system of TIP4P water with the Langevin thermostat set at 220K
- Change the thermostat temperature (instantaneously) to 270K
- Equilibrate the system at the new temperature

This experiment was repeated ten times (for good averaging), and then repeated for various combinations of linear and rotational thermostat weight. The performance of the thermostat can then be measured in terms of the relaxation time of potential energy, that is the time between changing the thermostat temperature, and the potential energy settling to the new equilibrium value. The results are shown in Figure 2.1.

We conclude that, judging the performance of the thermostat on the speed of relaxation to equilibrium, there is an optimal value for the thermostat weights. For very small weights, the coupling is so weak that the thermostat will take a long time to exert any effect. For very large weights, the strong perturbations exerted on the system seem to inhibit the path to equilibrium, though this is an empirical observation only; we have no conceptual physical explanation for this phenomenon.

The optimal thermostat has both translational and rotational weights of about the same magnitude. This provides justification for developing such a thermostat, since it shows that better performance can be achieved when all degrees of freedom are directly influenced by the thermostat.

The simulations for which optimal values of  $\gamma$  and  $\Gamma$  were obtained, as described above, were similar to those used in the cleaving method for this work, that is, the TIP4P model of water, in a simulation cell of comparable size. The optimal values determined here are the ones we then used throughout this work, and we are confident that they are appropriate.

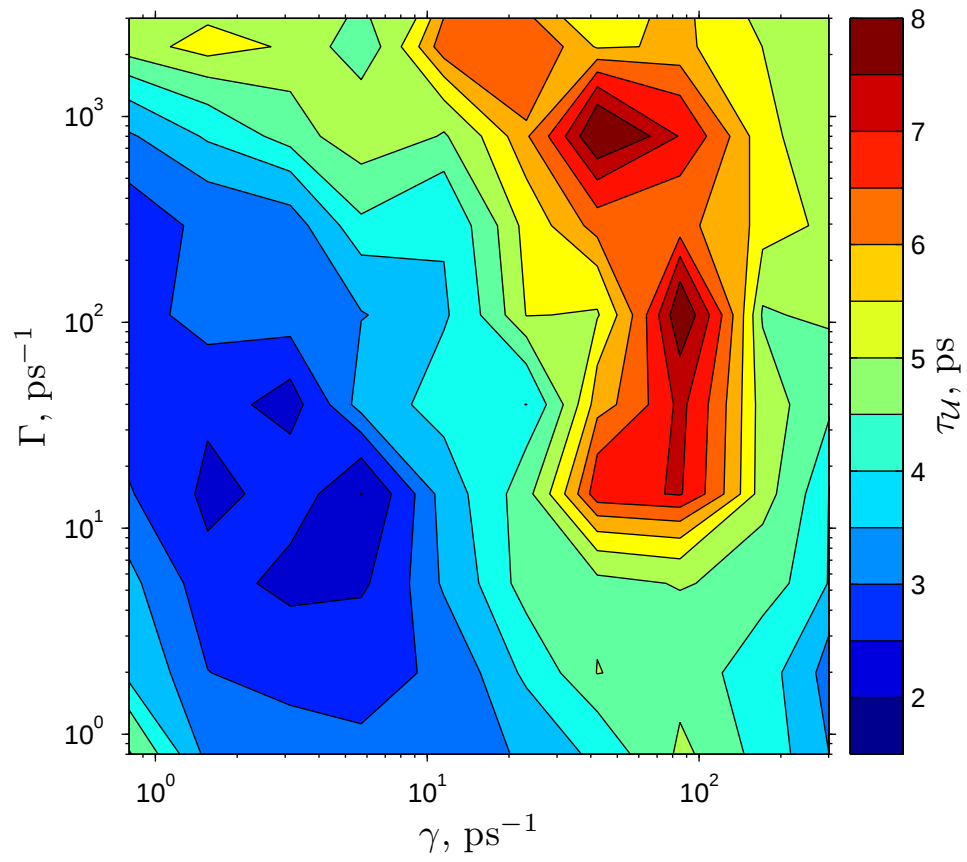


Figure 2.1: Performance of the Rigid Body Langevin Thermostat. Relaxation time of system potential is plotted against the thermostat parameters  $\gamma$  and  $\Gamma$ .

# CHAPTER III

## WATER AND ITS SIMULATION

The simulations in this work are done using one of the most common models of water, TIP4P, and its variant TIP4P-Ew. There are simpler models of water in common use, such as SPC/E and TIP3P, but those models do not reproduce the qualitative structure of the ice–water phase diagram; TIP4P does this reasonably well [30]. TIP4P was chosen as the simplest model of water which can be expected to give reasonable results when studying freezing phenomena.

### 3.1 The TIP4P Model

TIP4P [31] is a rigid model of the  $\text{H}_2\text{O}$  molecule with four interaction sites. Its geometry, which corresponds to the experimental gas-phase geometry, is illustrated in Figure 3.1. The interaction parameters are:

- a charge of  $+0.52e$  located at each hydrogen site,
- a charge of  $-1.04e$  located  $0.15\text{\AA}$  from the oxygen site, in the position indicated in Figure 3.1,
- a Lennard-Jones potential at the oxygen site, with width  $\sigma = 3.15365\text{\AA}$ , and depth  $\epsilon = 0.1550$  kcal/mol.

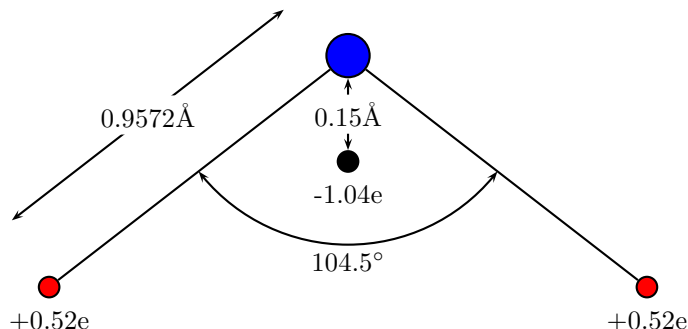


Figure 3.1: A diagram illustrating the geometry of the TIP4P water model

## 3.2 The TIP4P-Ew Model

TIP4P-Ew [17] is a more recent variant of TIP4P; the model has the same geometry, but the interactions are re-parametrized for Ewald Sums. Originally, electrostatic forces were truncated (see Section 2.2.3, page 2.2.3), and the parameters for the TIP4P model were calibrated so that the model matches the properties of real water as closely as possible. The TIP4P-Ew model has the parameters adjusted to match water as closely as possible when Ewald Sums (see Chapter 6, page 71) are used instead of truncation. The interaction parameters are:

- a charge of  $+0.52422e$  located at each hydrogen site,
- a charge of  $-1.04844e$  located as for TIP4P,
- a Lennard-Jones potential at the oxygen site, with width  $\sigma = 3.16435\text{\AA}$ , and depth  $\epsilon = 3.16435\text{ kcal/mol}$ .

## 3.3 Ice

Of the 16 known solid crystalline forms of ice [32], only the most common, ice  $I_h$ , is studied in this work. It has a proton disordered hexagonal crystal structure. The disordered structure means that, rather than being arranged in a regularly repeating pattern, there is a randomness inherent in the molecular orientation, within the constraints defined by the Bernal-Fowler ice rules [16]:

- The oxygen atoms form a hexagonal lattice
- Each oxygen has a single hydrogen bond with each of its four neighbouring oxygens
- Each oxygen is chemically bonded to two of its four neighbouring protons

The last of these rules is just a restatement of the fact that the crystal is composed of water molecules; the point is that there is precisely one hydrogen between each oxygen and its four nearest neighbours, two of which are chemically bonded with that oxygen in a water molecule, the other two with adjacent oxygens.

We consider three different cleaving planes of the Ice  $I_h$  crystal. These are the three simplest, and most commonly discussed cleaving planes. The cleaving method is repeated, and  $\gamma_{sl}$  estimated separately, for each of these planes. Picturing the ice crystal structure as horizontal layers of tessellated hexagons stacked vertically, the cleaving planes are:

- Basal Face: the basal face,  $\{0001\}$ , is obtained by cleaving the ice in the horizontal plane, that is, the ice is cleaved in the plane of a layer of the tessellated hexagons.
- Prismatic Face: the prismatic face,  $\{1\bar{1}00\}$ , is a vertical plane (perpendicular to the basal face), with horizontal component in the direction of any of the edges of one of the hexagons.
- $\{11\bar{2}0\}$  Face: this face is also perpendicular to the basal face, with horizontal component in the direction perpendicular to any of the edges of one of the hexagons.

### 3.3.1 Random Sampling of the Crystal Structure

Non-equilibrium methods estimate free energy from an average over many trajectories. The ice crystal in the simulations for this study consists of about 2,000 molecules. There are countless possible ice  $I_h$  crystal configurations (all satisfying the ice rules) which could be used. For such a small crystal size, different random configurations have measurably different thermodynamic properties, as illustrated in the discussion below.

Figure 3.2 shows system pressure for an ice crystal of the TIP4P-Ew (with Ewald Sums) model at ice-water co-existence conditions. Although the pressure fluctuates considerably over small timescales (a consequence of the tiny simulation volume), there is a clear and persistent pressure bias in the Y direction. A similar run, performed on a system identical in every respect apart from a different choice of crystal configuration (Figure 3.3), shows a different pressure bias, this time in the X direction.

One concludes from this that the simulation volume is too small for a single simulated ice  $I_h$  crystal to represent precisely the thermodynamic properties of ice  $I_h$  in general. To provide better sampling, a distinct crystal configuration is randomly generated for each trajectory. It should be remarked that it would not be possible to sample crystal structures in this way with methods such as thermodynamic integration, where the results are calculated from the simulation of a single system. This flexibility illustrates a subtle advantage of non-equilibrium methods when applied to disordered crystal structures.

It may be objected that these observations provide evidence that an isobaric simulation would be more suitable than the canonical ensemble which we decided to use. Had we used an isobaric ensemble, the procedure for calibrating the system (described in detail below) would also be much simplified. But there are other considerations which weigh against the use of such an ensemble. This point is discussed fully in Section 4.9 (page 64).

### 3.3.2 An Algorithm for Generating Proton Disordered Ice

A method is required for generating ice  $I_h$  crystals with random proton disorder. A Monte Carlo algorithm to do this has been devised by Buch [33].

First, a hexagonal lattice of oxygen atoms is generated, and a proton is placed between each pair of oxygens. It remains to assign a chemical bond between each proton and one of its two neighbouring oxygens. To start the process off, such a bond is assigned randomly to each proton. At this stage, oxygens may be chemically bonded to any number of protons between zero and four. To convert this to a crystal of water molecules, bonds are swapped until each oxygen is chemically bonded to exactly two protons. This is effected with a series of Monte Carlo moves. Each move selects a proton at random, and switches its bond to the opposite oxygen. Such a move is favourable (respectively unfavourable) if it brings the two oxygens closer to

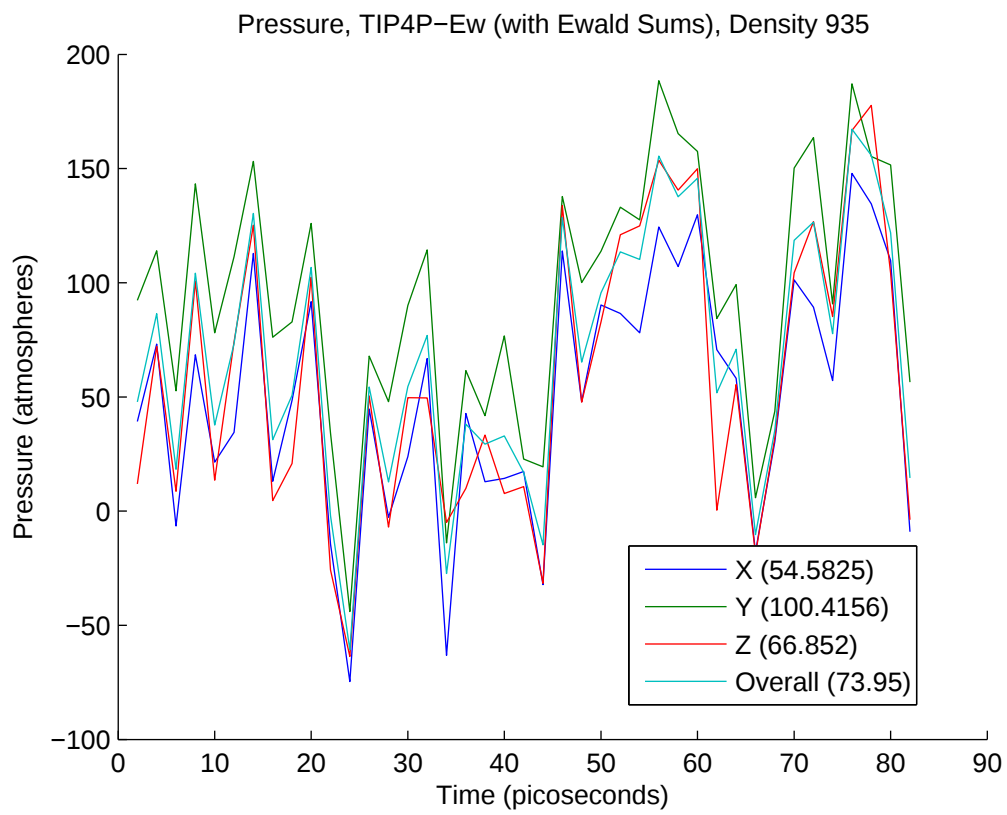


Figure 3.2: A graph of pressure for equilibrated ice  $I_h$ . Pressure is averaged over intervals of 2 picoseconds (the simulation timestep is 2 femtoseconds). Pressure is anisotropic, and greater in the Y direction.

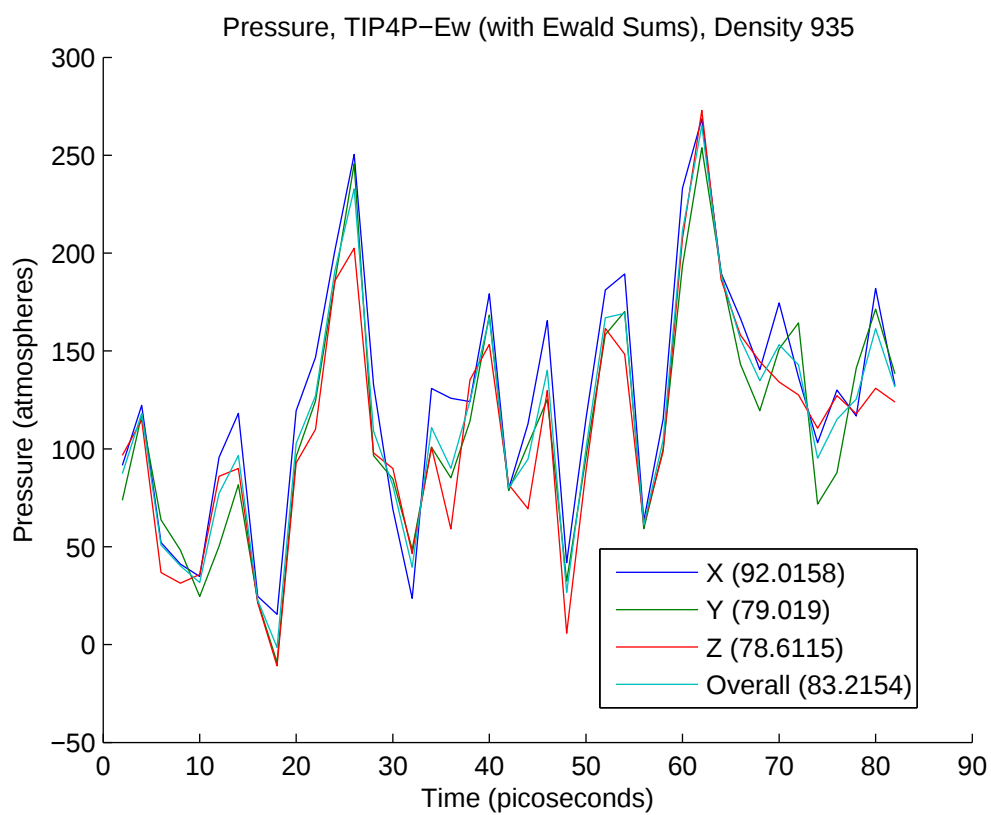


Figure 3.3: A graph similar to Figure 3.2, but with different proton disorder in the crystal. The anisotropy is now greater in the X direction, illustrating the sensitivity of pressure to proton disorder for this size of simulation cell.

(respectively further from) having, on average, two chemical bonds each. Or in the third case, the move is neutral. The acceptance rules for the move are:

- If the move is favourable, accept it.
- If the move is unfavourable, reject it.
- If the move is neutral, accept it with probability one half.

This simple brute force algorithm, though computationally intensive, is effective for the size of ice crystals used in this study (about two thousand molecules); a single random crystal structure is generated in about five minutes of computer time.

An additional selection was also imposed – for each starting configuration required, ten configurations were generated, the one with the lowest dipole moment selected, and the rest discarded. The dipole moment of different random structures was found to vary considerably, and this variation is just an artifact of the small number of the molecules in the simulation, since the dipole moment of bulk disordered ice  $I_h$  is zero. The effect of periodic boundary conditions on a small simulation cell will magnify the effect of any dipole moment ‘fluctuation’. By selecting systems with lower dipole moments we aim to minimise this undesirable effect, and best reflect the properties of a larger system of bulk ice.

## 3.4 Pressure Calibration

The simulations in this work are performed in the ‘canonical’ (or  $NVT$ ) ensemble, with the number of molecules, volume and temperature held constant.

To create an interface at co-existence conditions, ice and water systems are first prepared at the same temperature and pressure. Whereas temperature is controlled on the fly by means of a thermostat, pressure is calibrated a priori by adjusting the simulation cell volume. For the crystal, each dimension of the simulation cell must be calibrated so that pressure is isotropic. As noted in Section 3.3.1 (page 36), pressure anisotropy is sensitive to proton disorder in ice  $I_h$ , so the calibration for any particular system can only be approximate. To simulate normal ambient conditions, pressure is calibrated to 1 bar. However, it should be noted that the error in calibration is at least an order of magnitude greater than this (10-20 bar), so in practice, pressure is calibrated to zero within statistical error.

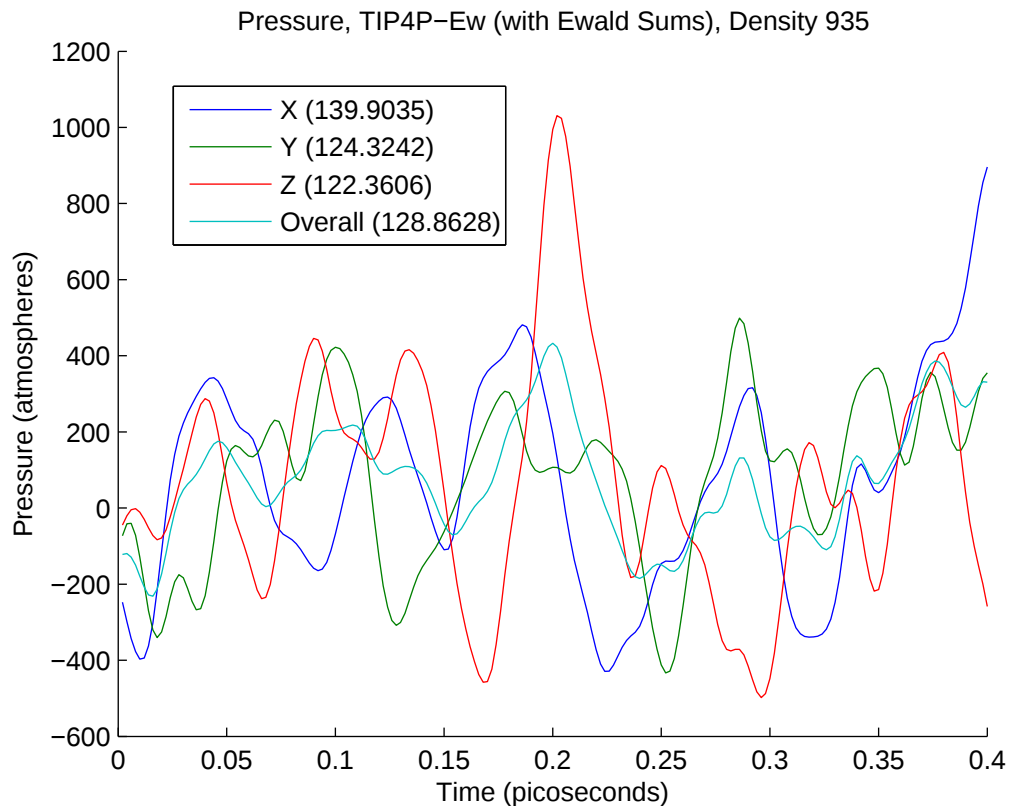


Figure 3.4: A graph of ice pressure at co-existence conditions. Instantaneous pressure at each time step is plotted, illustrating the degree of pressure fluctuation.

Since pressure is calibrated before temperature, the precise coexistence temperature is not known at this stage. A best estimate from published data is used. A small temperature adjustment may later be needed when temperature is calibrated (see Section 3.5, page 42); in practice such adjustments are found to have a negligible effect on the pressure.

As Figure 3.4 shows, instantaneous pressure fluctuates significantly. Long equilibration runs (1 or 2 nanoseconds) are needed for precise calibration.

For ice  $I_h$  the TIP4P-Ew (with Ewald Sums) model at the melting temperature 245 K, a density of 935 kg/m<sup>3</sup> was found to give a pressure of approximately 1 bar. This is in reasonable agreement with the density of 936 kg/m<sup>3</sup> previously obtained for ice co-existence of this model [34].

## 3.5 Temperature calibration

In order to determine the coexistence conditions for each water model, the direct coexistence simulation method [35, 36, 37] is used. In this method a heterogeneous system containing the two phases separated by an interface is allowed to evolve in a long simulation run. If the conditions of the simulation are not close to the coexistence conditions for the two phases, the system will evolve towards the phase which is more stable (i.e. the one with the lowest free energy), with the transformation between the phases taking place at the interface. In the system containing crystal and melt phases, one would observe melting (freezing) at the interface if the temperature were above (below) the melting temperature. This process is repeated for several adjacent temperatures to identify the coexistence temperature.

The system containing the two phases needs to be constructed. This is a straightforward process consisting of the following steps:

- A system of ice (with a roughly cubic simulation cell) is equilibrated at the specified temperature. The density of the system is adjusted to calibrate for pressure, as described in Section 3.4 (page 40).
- A system of water (again roughly cubic, whose simulation cell has identical x and y dimensions as the ice) is equilibrated and calibrated for pressure similarly, by adjusting the z dimension only.
- The two systems are combined by concatenating the simulation cells in the z direction, as illustrated in Figure 4.15.
- The molecules in the water system are compressed in the z direction to leave a 3Å gap between the ice and water systems. This prevents the system exploding due to overlapping molecules.
- The ice molecules are fixed in position (conceptually, they are given infinite mass), to prevent the ice melting while the water equilibrates.
- The system is then equilibrated for a short time with the ice molecules fixed, to allow the water to relax into the interface without disturbing the ice structure.
- The ice molecules are then released.

- The system is then further equilibrated for a short time to give the starting point.

Once prepared, the system is then equilibrated for a long period (5 nanoseconds or more). Any net melting or freezing can be observed as a gradual increase or decrease (respectively) in the total system potential energy.

An example of the use of this method can be seen in the graph showing the results for five different temperatures, for the TIP4P water model with discontinuous truncation, see Figure 5.1.

# CHAPTER IV

## THE CLEAVING METHOD

### 4.1 History of the method

The cleaving method was introduced by Miyazaki, Barker and Pound in the 1970s [38], for calculation of the liquid/vapour interfacial free energy. It was adapted to the solid–liquid interface by Broughton and Gilmer [8] in 1986. To date, it remains the only computational method for the direct calculation of solid–liquid interfacial free energy. Originally, it was applied to a system of truncated Lennard-Jones spheres.

The method was adapted for hard spheres by Davidchack and Laird [9] in 2000. The algorithm needed to be changed to accommodate the different nature of the time stepping algorithm for hard spheres. For Lennard-Jones spheres, the potential is continuous, and a numerical integrator yields an approximate solution to the set of ordinary differential equations describing the motion. For hard spheres, the potential is discontinuous, the velocities are piecewise linear, and the equations of motion are solved precisely (subject only to the errors inherent in floating point arithmetic), on a collision by collision basis.

Also at this time, the cleaving potential was improved. Broughton and Gilmer’s original potential was a repulsive plane, the strength of repulsion being dependent only on the perpendicular distance from the cleaving plane. This potential was smoothly introduced and removed at the start and end of the cleaving process by means of a coupling parameter. Davidchack and Laird used instead a pair of cleaving *walls*, constructed as crystal layers exactly matching the layers neighbouring the cleaving plane in the bulk crystal system. These walls are moved in and out of range at the start and end of the cleaving procedure, again by means of a coupling

parameter. When the cleaving is done with such walls, more accurate results are obtained: the cleaving potential fits naturally, by design, with the crystal structure at the cleaving plane, and hysteresis is considerably reduced.

As mentioned in Section 1.1 (page 1), the interfacial free energy,  $\gamma$ , of any solid–melt interface is dependent on the crystallographic orientation of the solid face in contact with the liquid, the extent to which the values of  $\gamma$  differ from each other being referred to as anisotropy. The adapted version of the cleaving method provided sufficient accuracy to distinguish the anisotropy for hard spheres. Values of  $\gamma = 0.62 \pm 0.01$ ,  $0.64 \pm 0.01$  and  $0.58 \pm 0.01 k_B T / \sigma^2$  were obtained for the (100), (110) and (111) face-centred-cubic crystal–fluid interfaces respectively.

In 2003, returning to the Lennard-Jones system [10], the accuracy of Broughton and Gilmer’s original result was improved so that, here too, the anisotropy was distinguished.

In 2005, the method was applied to a variety of inverse power potentials, for both body-centred-cubic and face-centred-cubic crystals [11]. The value of  $\gamma$ , and its anisotropy, were both found to increase with softer (that is, longer range) potentials. Also, it was observed that  $\gamma_{\text{bcc}} < \gamma_{\text{fcc}}$ , an observation consistent with experimental and theoretical observations. The nucleation of fcc crystals is known to take place via the initial formation of metastable bcc nuclei [39].

## 4.2 Outline of the Method

As noted in Section 1.1 (page 1), solid–liquid interfacial free energy,  $\gamma_{\text{sl}}$ , is the reversible work per unit area required to form an interface between solid and liquid.

The idea of the cleaving method is to simulate the formation of a solid–liquid interface, and calculate the reversible work performed on the system in order to effect this formation. Provided certain conditions are met (discussed below) this work is precisely the free energy of the interface formed.

Two separate systems of solid and liquid, prepared at coexistence conditions, are combined (by a four-step transformation process) into a single system, thus creating two interfaces at the boundaries where the systems are joined. Since both systems are maintained at coexistence conditions, the interfaces in the final system are stable, and no overall melting or freezing occurs.

The four steps of the transformation process are as follows:

**Step 1:** Cleave the solid system with a suitably chosen external potential (the *cleaving potential*) along a plane (the *cleaving plane*). The cleaving plane is positioned at a crystal layer within the solid system; it is this layer at which the interface will be formed.

**Step 2:** Cleave the liquid system in the same way. The position chosen for the cleaving plane in the liquid system is arbitrary. The cleaving potential is identical to that used for the solid system. The effect is the formation of a crystal-like layer within the liquid at the cleaving plane. The molecular positions and orientations within this layer match correspondingly with the solid system at the cleaving plane. The layer also acts as a barrier ~~through~~ which the liquid particles cannot cross.

**Step 3:** Merge the two systems by gradually rearranging the boundary conditions to allow interaction between the solid and the liquid across the cleaving planes while maintaining the cleaving potential.

**Step 4:** Remove the cleaving potential from the combined system.

Provided the initial isolated solid and liquid systems have been equilibrated at the solid-liquid coexistence conditions, the only result of the above transformation process is the creation of the solid-liquid interface. Therefore the sum of the (reversible) work performed on the system in the above four steps constitutes the interfacial free energy  $\gamma_{sl}$  times the area of the two solid-liquid interfaces which are created in the process.

This is a delicate and complex procedure. The method is only valid if all the steps are performed reversibly, which means the transformation must be done slowly. However, if any freezing or melting were to occur during the transformation, this would also invalidate the method, so it is crucial that precise co-existence conditions are maintained.

## 4.3 Preventing Crystal Drift

As mentioned in Section 4.2 (page 45), the position of the cleaving potential is chosen to match the crystal layer in the ice system which is to be cleaved. At certain stages in the process, the potential is not present, and the crystal would then be free to drift. Any such drift must be prevented, otherwise the position of the potential would not

match the positions of the molecules, making it impossible to cleave the crystal. Of course, the crystal can not drift unless there is an overall linear momentum in the system, and the usual way of preventing such drift is to remove any overall linear momentum at the start of the simulation. But such an approach will not work in this case because of the effect of the external potentials. The presence of a stochastic thermostat will also cause the overall linear momentum to fluctuate. So we need a method of preventing the drift that these external influences could otherwise introduce.

To prevent any drift of the crystal system, a crystal layer is pinned in place. The pinned layer is the layer parallel to the cleaved layer which is mid-way between it (the cleaved layer) and its periodic image. Each molecule in the pinned layer is attached by its centre of mass to its ideal position by a harmonic spring. The strength of the spring was set to  $4 \text{ kcal}/\text{\AA}^2/\text{mole}$ , a value determined by trial and error to be as small as possible while remaining effective (perhaps a better approach would have been to choose a value corresponding to the natural vibration frequency of an ice molecule, but we did not explore this). This pinning potential remains in place throughout the cleaving process, and, providing the crystal system is sufficiently large in the direction normal to the interface, has no effect on the computed interfacial free energies.

## 4.4 The Cleaving Potential

The cleaving potential serves two purposes: firstly, it induces a matching alignment of molecules in the two isolated systems in order that they may be fused smoothly, and secondly, it prevents any molecules from crossing the cleaving planes during the fusing process (such crossings must be prevented so that the process of rearranging the boundary conditions in Step 3 is well defined). Also, in order to have a short transformation path, the cleaving potential should perturb the system as little as possible. Both purposes are served if the cleaving potential is designed to promote the formation of ice crystal layers at the cleaving plane.

In the previous implementations of the cleaving method, applied to the pair potentials of hard or soft spheres, the cleaving potential was purely repulsive, tailored to mimic the interaction of liquid particles with layers of crystal particles at the interface. The resulting ‘wall’ of potential was then gradually moved into range [9,

10]. This ‘moving walls’ concept, designed only for monotonic pair-potentials, can not be used with more complex molecular potentials which combine Lennard-Jones and electrostatic interactions, and where attractive forces play an essential role in determining the crystal structure. The task of designing the cleaving potential for molecular systems is further complicated by the need to induce specific orientations of the molecules within the crystal structure.

To address these new needs of a cleaving potential for a molecular system, we changed the potential from moving, repulsive *walls* to fixed, attractive *wells*. Instead of gradually moving the walls into position, the wells are gradually switched on. The wells are located at the ideal crystal positions near the cleaving plane, and attract molecules to the lattice sites. In addition, they induce the correct *rotational orientation* on each molecule for its position in the crystal.

For a rigid molecule with center-of-mass coordinates  $\mathbf{r}$  and orientational coordinates  $\mathbf{q}$  (e.g. rotation matrix, Euler angles, or quaternions), the cleaving potential has the following generic form:

$$\Phi(\mathbf{r}, \mathbf{q}) = \sum_j \phi(|\mathbf{r} - \mathbf{R}_j|) \theta(\mathbf{q}, \mathbf{Q}_j), \quad (4.1)$$

where  $\mathbf{R}_j$  is the position of the potential well  $j$  and  $\mathbf{Q}_j$  is the desired orientation of a molecule within the well.

Therefore, the pair potential for each well-molecule pair is the (arithmetic) product of a *translational* and a *rotational* component. The translational component,  $\phi$ , depends only on the distance of the molecule’s center of mass from the well. The rotational component,  $\theta$ , depends on the orientations of well and molecule.

Typically,  $\phi(r)$  is a simple well function with a minimum (negative) value  $-d_w$  (the ‘well depth’) at  $r = 0$  and a finite range  $r_w$ , i.e.  $\phi(r) = 0$  for  $r \geq r_w$ . In this work we employed a simple polynomial function:

$$\phi(r) = d_w [(r/r_w)^2 - 1]^3 \text{ for } r < r_w. \quad (4.2)$$

To induce the desired orientation,  $\theta(\mathbf{q}, \mathbf{Q})$  should be a smooth function which is positive when a molecule is aligned with the desired orientation (i.e.  $\mathbf{q}$  is close to  $\mathbf{Q}$ ) and negative when the molecule is misaligned. The overall result is a potential which attracts molecules with good alignment, and repels those with bad alignment, and

furthermore exerts a torque on the molecules in the direction of perfect alignment. We used the following in all our simulations:

$$\theta(\mathbf{q}, \mathbf{Q}) = \mathbf{n}(\mathbf{q}) \cdot \mathbf{n}(\mathbf{Q}) \quad (4.3)$$

where  $\mathbf{n}$  is a unit vector in the direction of the molecule’s ‘principal axis’ that links the oxygen to the mid-point of the hydrogens (i.e. aligned with the molecule’s dipole moment). Note that the torque induced by  $\theta$  only influences two of the three rotational degrees of freedom; our studies confirm that this is sufficient inducement for the molecule to find its correct orientation. Furthermore, to induce the third degree of freedom would increase the complexity of the well potential significantly, since the symmetry of the water molecule means that two formally distinct orientations are physically identical, and the potential must favor both equally to ensure proper sampling of the phase space.

## 4.5 Step 1 – Cleaving the Ice System

As remarked in Section 3.3.1 (page 36), different configurations of ice  $I_h$  crystal are used for different trajectory starting points. For each trajectory, a crystal structure is generated using the algorithm described in Section 3.3.2 (page 37). The dimensions of the simulation cell are adjusted to match the pressure calibration, as described in Section 3.4 (page 40).

A single crystal layer is then pinned, as described in Section 4.3 (page 46).

The molecules are located at their ideal crystal positions, and are given initial velocities from a Maxwell distribution in order to set the initial temperature to  $170K$ . The exact initial temperature is not significant: it should be sufficiently below the melting point to ensure the stability of the crystal structure while it settles down. Both translational and rotational velocities are set, the translational velocities being adjusted so that the overall momentum of the system is zero with respect to the simulation cell. A thermostat is introduced, and the thermostat parameters are altered so as to gradually increase the temperature to the melting point over a period of about 50 picoseconds. The thermostat is then set to maintain the system at the melting point, and the system is equilibrated thoroughly, for about 0.5 nanoseconds.

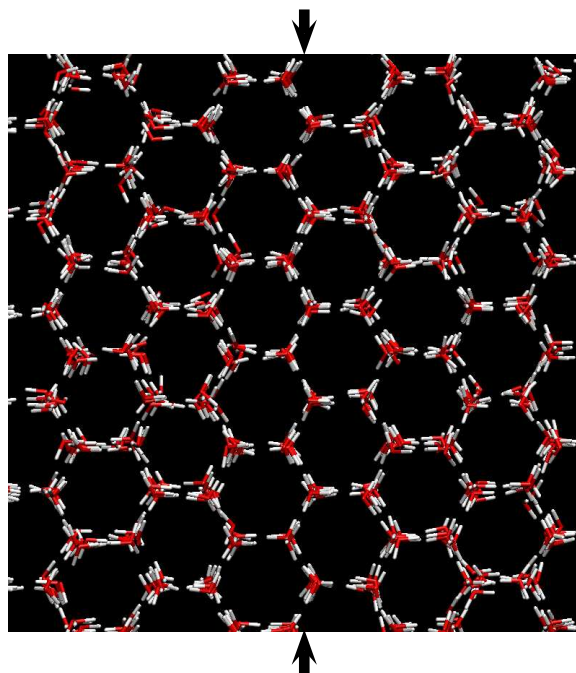


Figure 4.1: A graphical snapshot of the cleaved ice system. The arrows indicate the cleaving plane.

Once equilibration is complete, wells are smoothly introduced at the sites of each molecule in the cleaving layer. Each well induces its molecule to occupy its ‘ideal’ position and orientation in the crystal structure, that is, the potential is designed to match the structure of the crystal layer being cleaved.

A snapshot of the crystal after cleaving is shown in Figure 4.1. In this Figure, the normal vector to the cleaving plane is the horizontal axis, and the cleaving plane is identified by the arrows. The molecules in the cleaving plane are seen to be more tightly located at their lattice positions under the influence of the cleaving potential.

## 4.6 Step 2 – Cleaving the Water System

A convenient method of obtaining an initial sample of water in simulation is to melt ice. An ice crystal is placed in the simulation cell. The  $x$  and  $y$  dimensions of the simulation cell are scaled to match the ice cell prepared in Section 4.5 (page 49). The  $z$  dimension is adjusted for the density previously calibrated for water at a pressure of 1 bar.

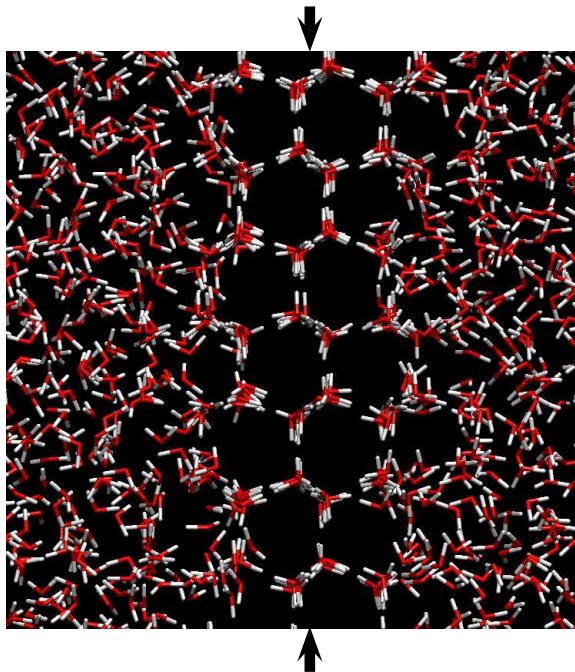


Figure 4.2: A graphical snapshot of the cleaved water system. The arrows indicate the cleaving plane.

The temperature is set to  $2000K$  (an arbitrary value high enough to melt the crystal in a few picoseconds) in the same manner as described in Section 4.5 (page 49). The temperature is smoothly reduced by means of a thermostat to the freezing point over about 50 picoseconds, after which time, the sample is thoroughly melted. The thermostat is then set to maintain the system at the freezing point, and the system is equilibrated thoroughly, over about 0.5 nanoseconds.

Once equilibration is complete, wells are smoothly introduced. The well positions and orientations are identical to those used to cleave the ice system, except for the  $z$ -alignment of the cleaving wall itself, which is arbitrary.

The wells induce the formation of a single crystal layer within the liquid. The effect is illustrated in the snapshot of the water system after cleaving (in this example, the prism orientation of ice  $I_h$ ), Figure 4.2. As before, the cleaving plane is identified by the arrows. The molecules in the cleaving plane are seen to arrange themselves into a crystal bilayer. Some additional freezing in the region of the cleaving plane can also be clearly seen in the figure.

As has been found in previous studies [10, 11], this step is the most prone to hysteresis. Creating a structural ordering in the liquid under the influence of an ex-

ternal potential at co-existence conditions is the principal source of irreversibility in the whole of the cleaving method. This problem was found to be particularly severe for water, as can be clearly seen in Figure 4.3. The graph shows the ‘work paths’ for individual trajectories, forward and reverse. The ‘work path’ is the derivative of the cleaving potential with respect to  $\lambda$ ,  $\partial U/\partial\lambda$ , plotted against  $\lambda$ . The integral of this function gives the work performed for the trajectory, which in turn contributes to the estimate of the interfacial free energy  $\gamma$ ; when the forward and reverse paths diverge, the integrals differ significantly, and  $\gamma$  can not be determined with any accuracy.

A graph of the average paths of the forward and reverse trajectories is shown in Figure 4.4. The path is clearly not reversible within computational timescales; there is a clear divergence between forward and reverse paths.

A histogram showing the distribution of the estimates of  $\gamma$  for each trajectory is shown in Figure 4.5. As can be seen from the figure, there is no overlap between forward and reverse estimates. The BAR estimate (Eq. 2.16) is shown on the figure, but the corresponding error bar (Eq. 2.17) is omitted from the figure as it is too large to display.

The hysteresis was found to be very persistent and could not be removed by slowing down the switching process.

The hysteresis was alleviated by reducing the interaction potential of the molecules. Reducing the potential, equivalent to heating up the system [40], moves it away from ice–water co-existence conditions. Scaling the potential is more convenient within the cleaving method, since it can be achieved simply by multiplying the molecular interaction potential by a coupling parameter  $\lambda$ . The scaling work can then be calculated from Eq. (2.15).

When the cleaving wells are introduced into a system with the potential reduced by 30%, there is no hysteresis, as can be seen in Figure 4.6. Forward and reverse trajectories can be seen to overlap throughout the cleaving path. The mean forward and reverse trajectories are shown in Figure 4.7. Even when averaged, the forward and reverse trajectories show good overlap. We also used a varying trajectory speed in this step; we slowed down the trajectory in the region of potential hysteresis,  $0 \leq \lambda \leq 2.2$ , for better reversibility, whereas over the remaining region,  $2.2 < \lambda \leq 1$ , we could safely increase the speed without any loss of reversibility. The slower trajectory speed can be seen in the figure as a denser path, since in these figures, the interval between plot points is proportional to number of time steps. We have

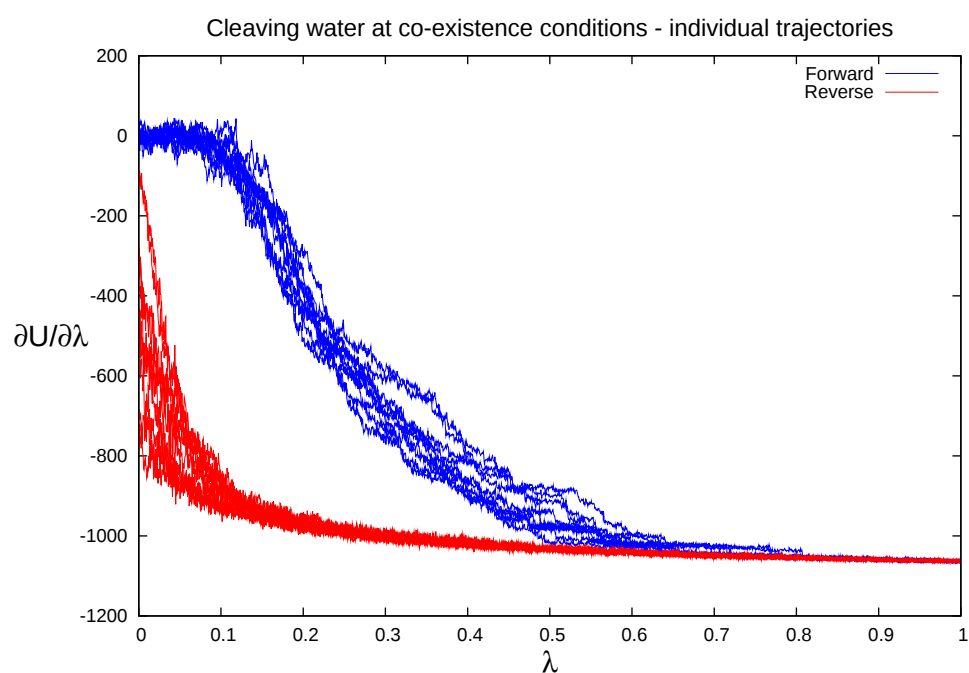


Figure 4.3: A graph illustrating the hysteresis problem for cleaving TIP4P water at co-existence. The ten forward and ten reverse trajectories are plotted separately.

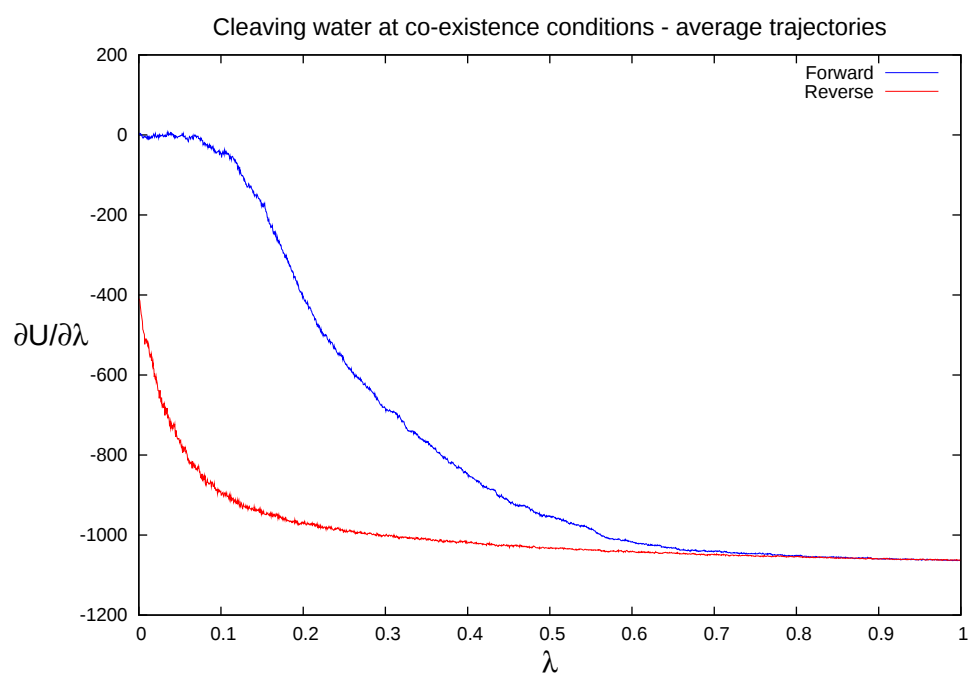


Figure 4.4: A graph showing the mean forward (reverse) trajectory path for the ten forward (reverse) paths shown in Figure 4.3.

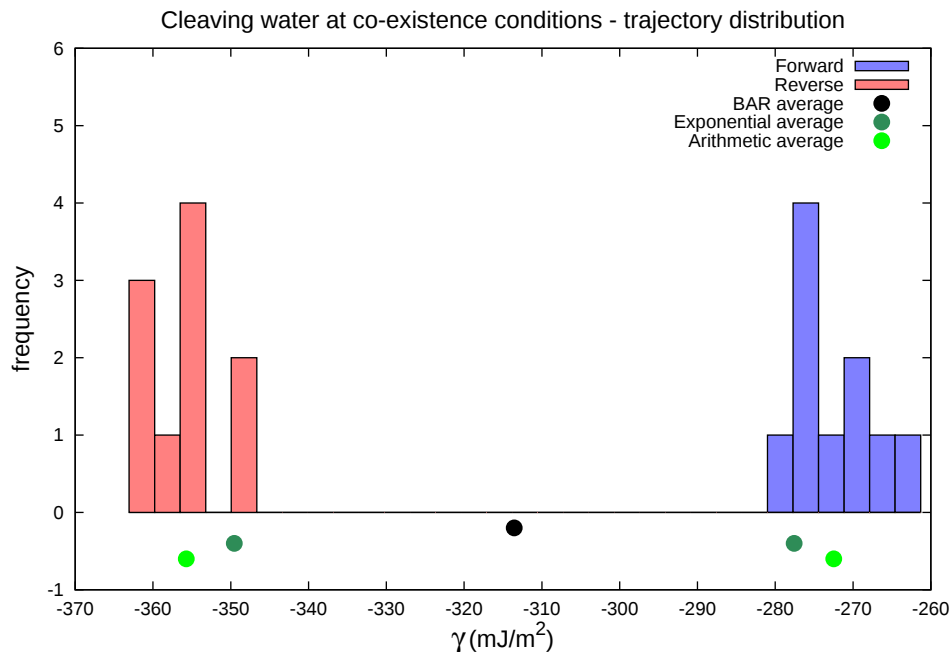


Figure 4.5: A histogram showing the distribution of ‘trajectory work’ for the trajectories shown in Figure 4.3.

varied the trajectory speed in this way in various places throughout the cleaving method, wherever we found regions of low accuracy.

The distribution of ‘trajectory works’ is shown in Figure 4.8. There is now some overlap between the work distributions of the forward and reverse trajectories. Since the forward and reverse trajectories provide (on average) upper and lower bounds on the free energy, such overlap is a good visual indication that the free energy is estimated with good accuracy. The BAR estimate (Eq. 2.16) and its error estimate (Eq. 2.17), indicated in the figure, confirm that the estimate is reasonable.

Of course, the reducing and restoring of the potential must also now be taken into account of the contribution to the energy estimate for step 2. To calculate the cleaving free energy at co-existence conditions using this ‘potential scaling’ technique requires three separate stages:

- Reduce the interaction potential of the (uncleaved) water system by 30%
- Cleave the (reduced-potential) water system by introducing the wells
- Restore the potential of the (cleaved) water system to its full value

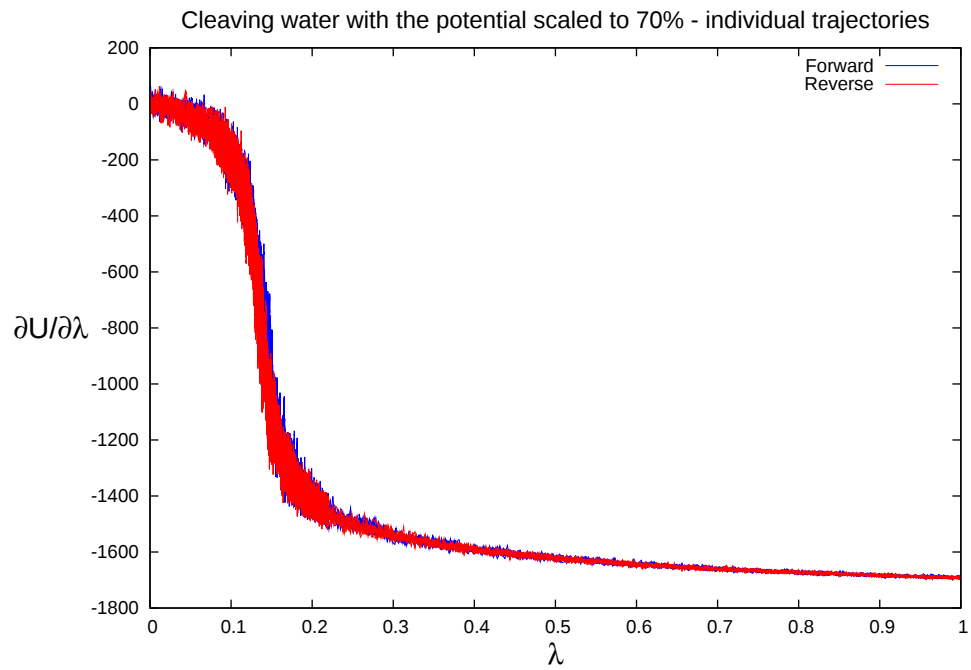


Figure 4.6: A graph illustrating that cleaving water at 70% potential solves the hysteresis problem.

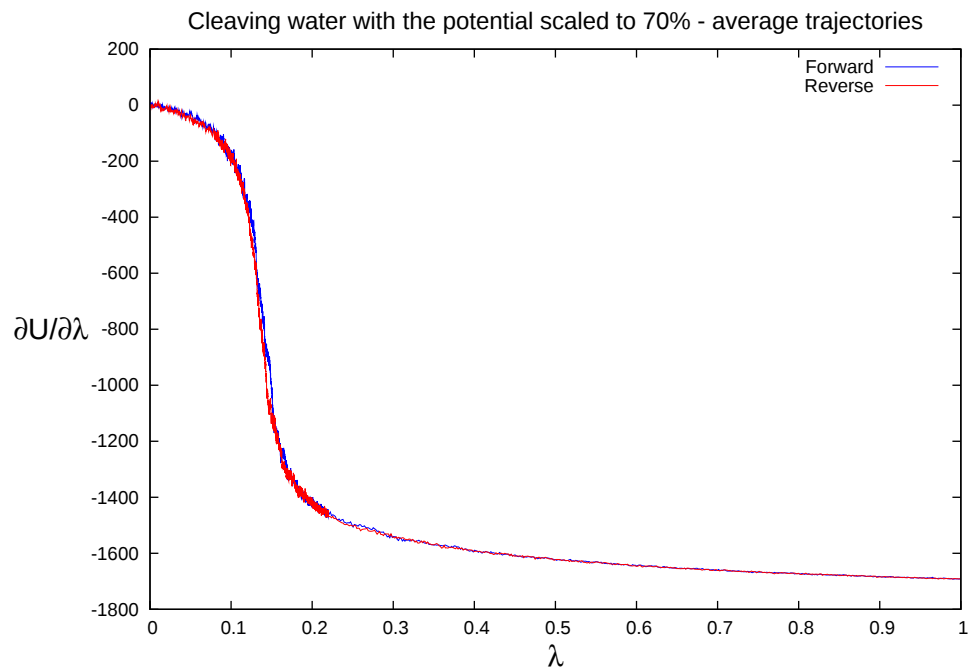


Figure 4.7: A graph showing the average trajectories from Figure 4.6.

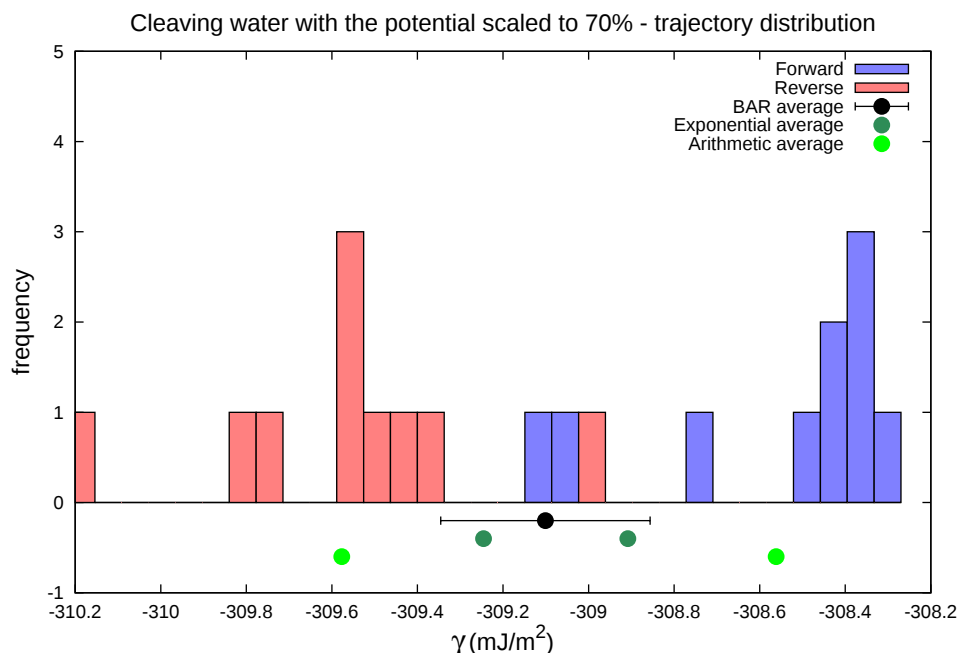


Figure 4.8: A histogram showing the distribution of ‘trajectory work’ for the trajectories shown in Figure 4.6.

The free energy for each stage is calculated (using similar techniques as before), and the total free energy of cleaving at co-existence is the sum of the three individual free energies. Graphs are shown for reducing the potential (figures 4.9, 4.10 and 4.11), and restoring the potential (figures 4.12, 4.13 and 4.14). There remains some hysteresis in the final stage (restoring the potential), as the cleaved system approaches full-potential (and therefore co-existence conditions). Despite slowing down the trajectories in this region, a slight hysteresis is still present, although it is now far less severe than the original cleaving hysteresis, and the forward and reverse work values are close enough for free energy to be calculated with reasonable accuracy.

## 4.7 Step 3 – Merging the Systems Together

Figure 4.15 illustrates the procedure for combining the systems, which is achieved by adjusting the interaction potential between molecules which interact ‘across’ the cleaving planes. Molecules on either side of the cleaving plane are separated in this

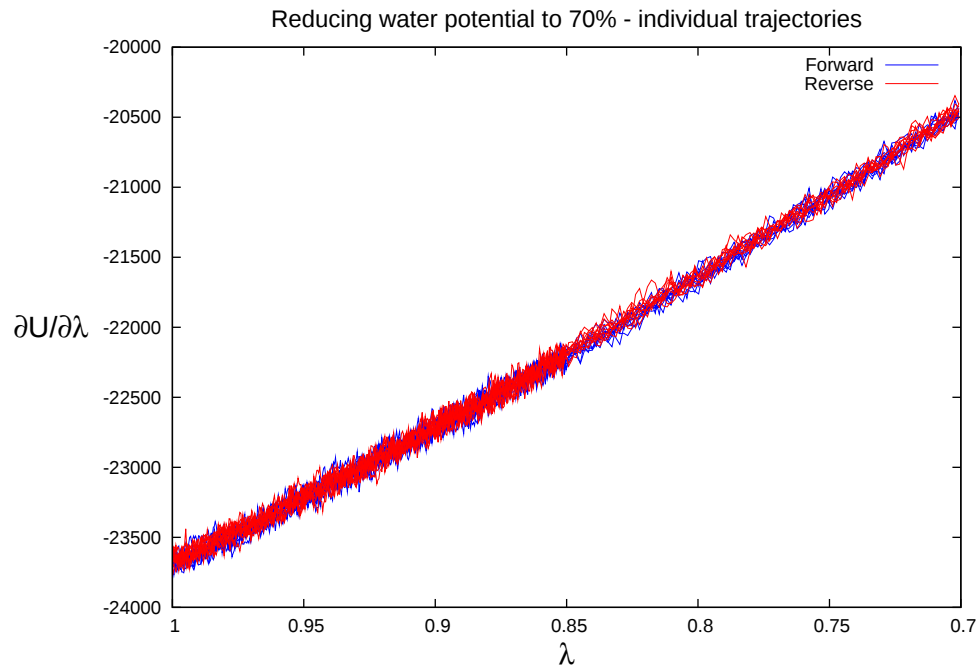


Figure 4.9: A graph showing the trajectory ‘work paths’ for reducing the potential to 70% in the uncleaved water system.

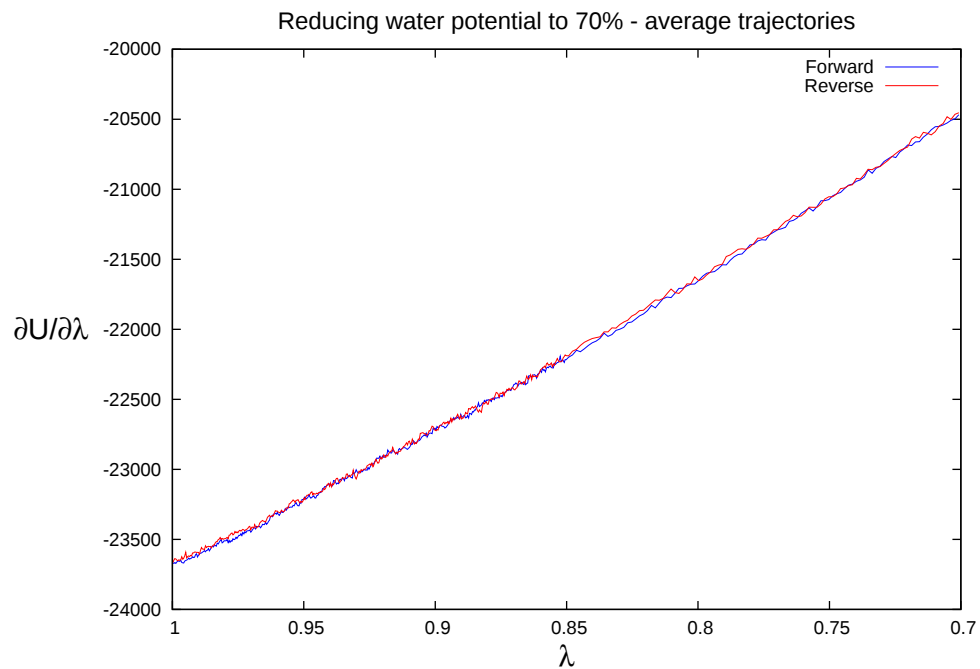


Figure 4.10: A graph showing the mean paths (forward and reverse) for the trajectories shown in Figure 4.9.

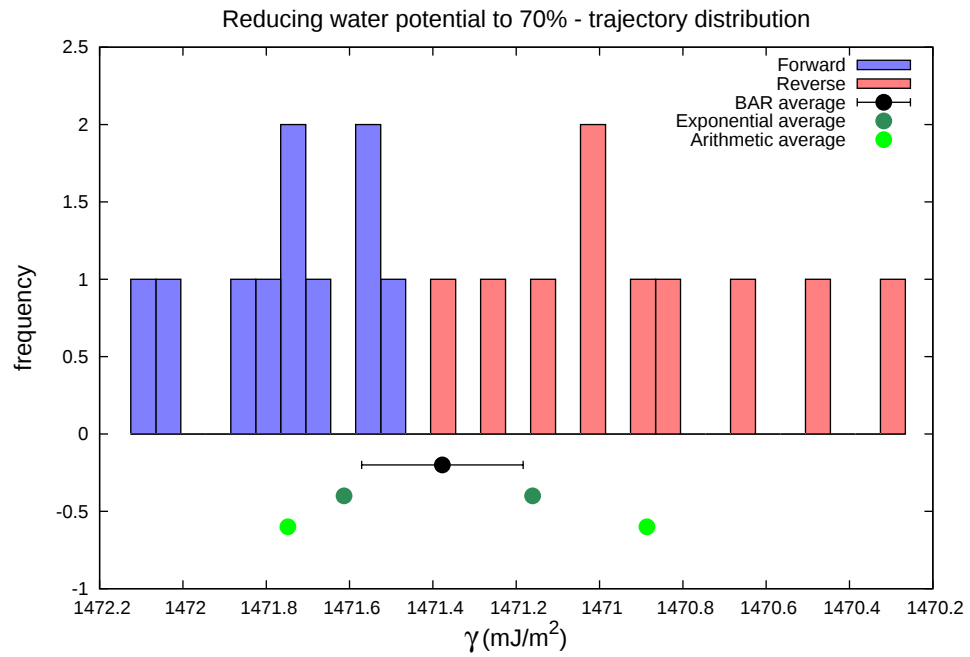


Figure 4.11: A histogram showing the distribution of ‘trajectory work’ for the trajectories shown in Figure 4.9.

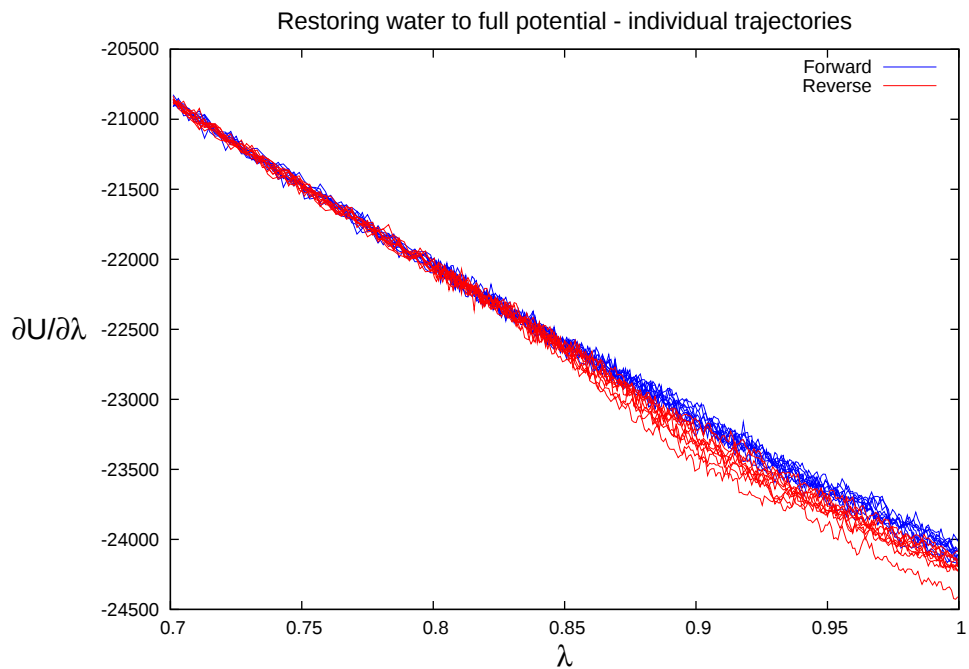


Figure 4.12: A graph showing the trajectory ‘work paths’ for the restoration of full potential to the cleaved water system. The hysteresis less severe than that of Figure 4.3.

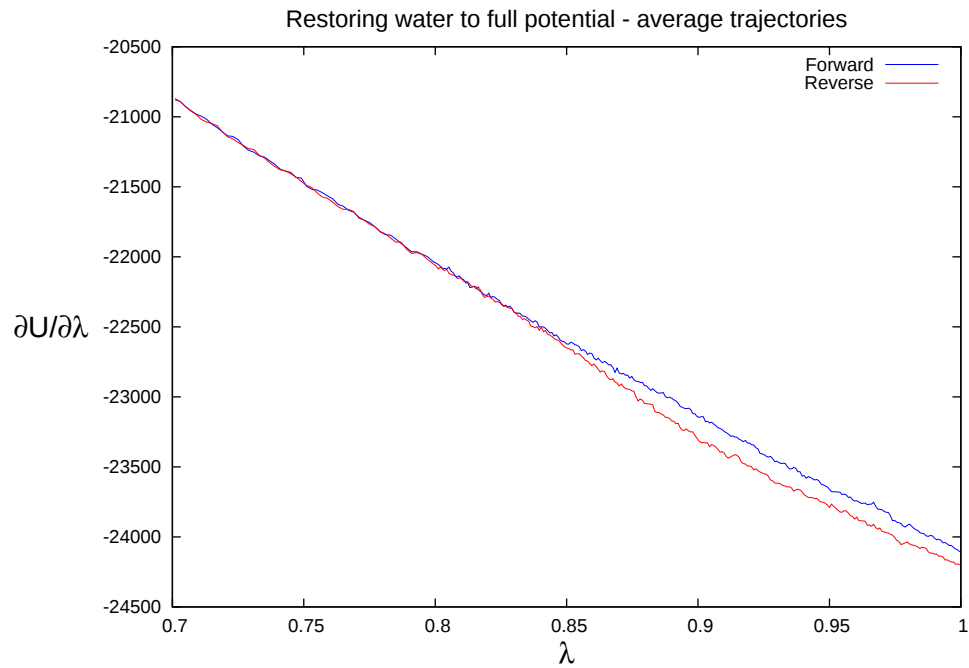


Figure 4.13: A graph showing the mean forward (reverse) trajectory path for the ten forward (reverse) paths shown in Figure 4.12.

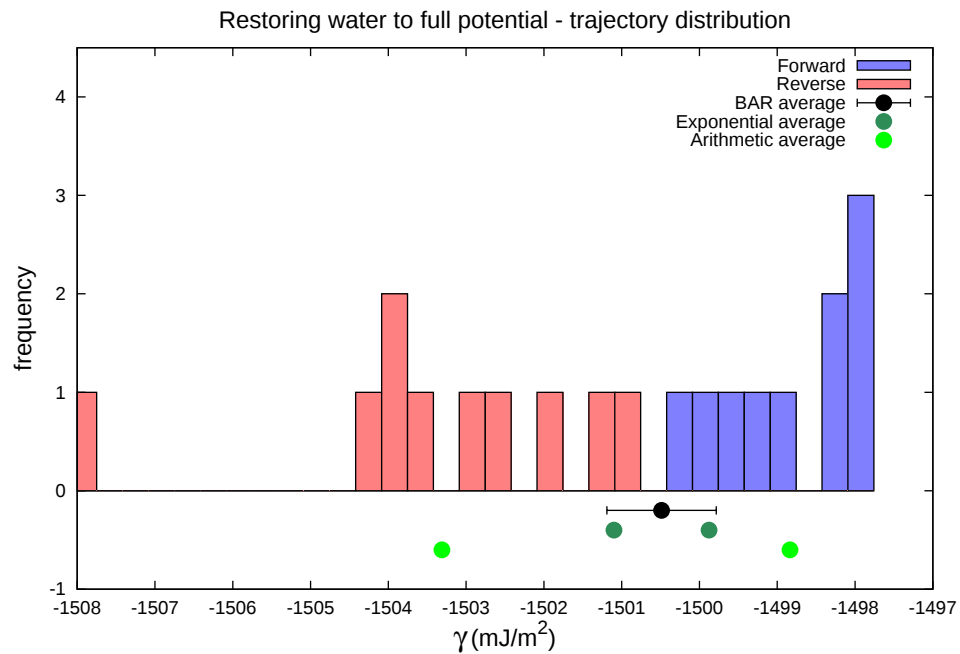


Figure 4.14: A histogram showing the distribution of 'trajectory work' for the trajectories shown in Figure 4.12.

step. Referring to the labelling in the figure, interactions  $I_1 \leftrightarrow I_2$  and  $W_1 \leftrightarrow W_2$  are smoothly switched off, while interactions  $I_1 \leftrightarrow W_2$  and  $W_1 \leftrightarrow I_2$  are smoothly switched on. This switching is performed via a coupling parameter  $\lambda$ . The potential  $U$  is defined by:

$$U(\lambda) = (1 - \lambda)(U_i + U_w) + \lambda U_{iw}, \quad (4.4)$$

where  $U_i$  and  $U_w$  are the molecular interaction potentials of separate ice and water systems and  $U_{iw}$  is the potential of the combined system. This (non-physical) switching of potentials transforms the two isolated systems into a single system with interfaces at the cleaving planes. The transformation is smooth (reversible) only because the two isolated systems have been prepared to match each other at the cleaving planes.

The approach relies on molecules not crossing from one side of the cleaving plane to the other once the wells are in place: if any molecule did so during this step, its position would become ambiguous, and in any case, either choice would result in discontinuity of forces.

The wells have been calibrated to be strong enough so that after cleaving, a single molecule permanently occupies each well. The simulation software monitors the molecules in occupation at each well, and checks that no such molecule is displaced within the cleaved system. It also checks that other, free molecules do not cross the cleaving plane. Test simulations confirmed that well-occupying molecules retain their occupation permanently, and form a potential energy barrier sufficient to prevent the crossing of other molecules, for all three crystal faces.

Note that a molecule occupying a well on one side may cross over for short periods from time to time as a result of normal thermal fluctuations. This does not constitute a change of sides as regards the interaction calculations described above. A table is maintained, recording which side each molecule is assigned to, where this assignment is based on the molecule's long-term position in the  $z$  direction, and may not always correspond to its instantaneous physical co-ordinates.

A snapshot of the merged system is shown in Figure 4.16.

### 4.7.1 Reversibility of Step 3

Some persistent hysteresis was observed in step 3, which had not been observed in the previous applications of the method to hard and soft spheres. Initially, we tried

to remove this by slowing down the trajectories. After much experimentation with slower trajectory speeds, we concluded that the hysteresis was persistent irrespective of the trajectory speed. To investigate this further, samples at the mid-point of the trajectory were taken from forward and reverse trajectories, and equilibrated. The forward and reverse runs equilibrated to different, apparently stable states, however long they were equilibrated for.

We remain unsure of the exact reason for this phenomenon, but the following explanation seems a plausible conjecture. The introduction of the wells in step two causes some additional crystal growth on either side of the wall (this much is certain, and can be observed by visual examination of the system at the end of step 2, Figure 4.2). The crystal structure is proton disordered; as the systems are merged in step 3, proton configurations adjacent to the frozen water layers change, and may be somewhat less favourable to the crystal structure as a whole, causing some minor irreversible rearrangement or melting in the water-side crystal configuration. Both orderings are meta-stable within the water-only system, and have somewhat different energies. If this conjecture is correct, then the method needs to be adapted for step 3 to be reversible. We decided to alter the ‘cooling down’ phase of step 2 so that the potential is only restored to 85% (rather than 100%). Step 3 is then performed with the water potential at 85%, and the water potential is only restored to 100% during step 4. In this way, the water system is less inclined to nucleate any ice-like layers adjacent to the cleaving wall during steps 2 and 3.

This conjecture could in principle be verified by checking the molecular configurations programmatically, but we have not attempted this. Whether or not the conjecture is correct, the modification to the method which was motivated by it, as described above, was implemented, and it successfully removed the hysteresis.

## 4.8 Step 4 – Removing the Wells

For the final step, it remains to remove the wells (which were introduced in steps 1 and 2, and kept in place throughout step 3), and to fully restore the potential of the water system. These two actions are performed simultaneously. By removing the wells while the final 15% of potential is restored to the water system, the combination of strong wells and coexistence conditions (which can encourage excess freezing in the water) is avoided.

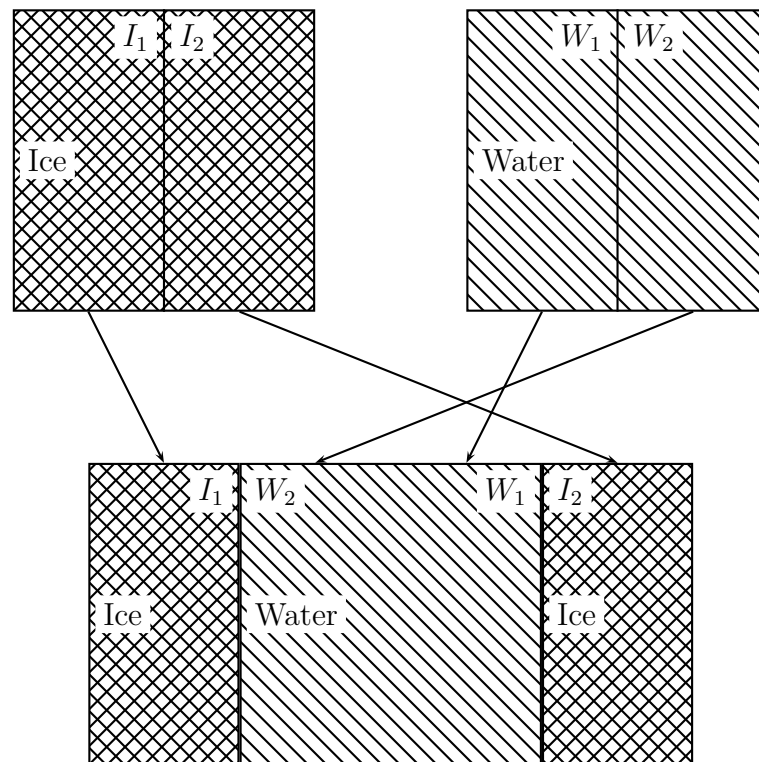


Figure 4.15: A diagram illustrating how the two isolated systems, with periodic boundary conditions, are merged into a single system. Two ice–water interfaces are ‘created’ at the cleaving planes.

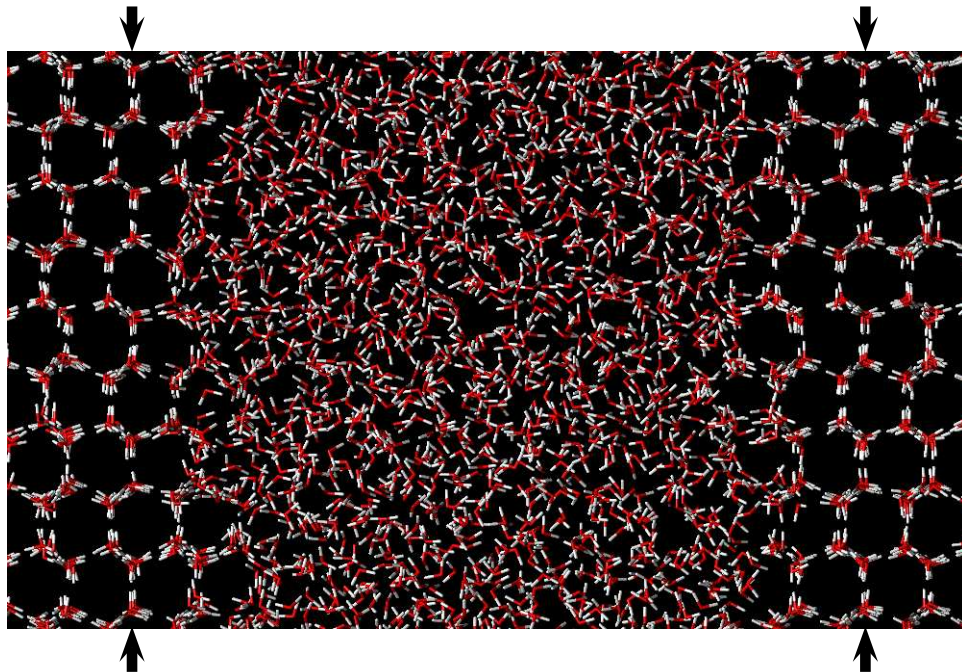


Figure 4.16: A graphical snapshot of the merged ice-water system. The arrows indicate the cleaving planes.

#### 4.8.1 Reversibility of Step 4

Another irreversibility, for a new reason, occurs in step 4. After the wells have been removed completely, the interface will naturally ‘wander’: even at co-existence conditions, there is no reason to expect the position and shape of the interface to remain constant over time. The overall ice–water balance remains constant, but the interface is no longer locked to the cleaving plane, and in general its shape and form will fluctuate. Therefore after the wells have been removed, and the system equilibrated, re-inserting the wells reversibly is impossible.

The best solution we have found to this problem is something of a compromise – by experimental trial and error, the lowest level of well strength at which the interface would still remain fixed in the position defined by the wells was found. This turns out to be 25%. Step 4 is then split into two:

1. Step 4a Reduce the well strength to 25% while simultaneously restoring the water potential to 100%.
2. Step 4b Remove the remaining 25% of the well strength.

Step 4a is reversible, and is treated as before. Step 4b is essentially irreversible, and is now as small as possible (in terms of its contribution to the free-energy). Step 4b is performed in the forward direction only. To compensate for the lack of reverse trajectories, the forward trajectories are run at several different speeds, and the averages extrapolated to estimate the free energy contribution. Additionally, exponential averages (2.4.1, page 21) are computed for each speed. This provides a further check against any systematic errors. Since, according to the , the exponential average converges to the free energy for any trajectory speed, the exponential averages should be consistent with the extrapolated value.

## 4.9 The Choice of Ensemble

All simulations were performed in the canonical ensemble, that is, at constant volume. The decision to use the canonical ensemble requires some justification. A crucial feature of the cleaving method is that ice–water coexistence conditions are maintained throughout the process. The obvious choice for such a requirement would be an isobaric ensemble, in which the volume of the simulation cell varies, and temperature and pressure are maintained at coexistence conditions. The use of the isobaric ensemble would also simplify the calibration of the system described in Section 3.4 (page 40); the two-stage calibration process would reduce to one stage, calibrating for the coexistence temperature while a barostat maintains constant pressure. On the other hand, the calculation of  $\gamma_{sl}$  would need to be adjusted to account for the work required for any possible overall change in system volume.

However, aside from this additional computational adjustment, there is a more serious problem in the application of the isobaric ensemble to the cleaving method. An isobaric ensemble allows any amount of freezing or melting to take place: the system volume will adjust to accommodate the expansion on freezing, or contraction on melting. Any overall freezing or melting during the method will invalidate the results.

A constant volume simulation provides a natural barrier to freezing or melting, since, for example, freezing is resisted by the resulting increase in density of the remaining liquid.

It could be objected that, since the simulation is supposed to be performed at precise coexistence conditions, freezing or melting should not occur in any case, and

this objection would be valid were it not for the influence of the external potentials during the cleaving method. For example, during the cleaving of water at step 2 (Section 4.6, page 50), wells are introduced into water at coexistence conditions. These wells encourage freezing, and over enough time would act as a seed to freeze the entire cell to ice – if the water (without the wells) is precisely at coexistence, the constant presence of wells in crystal formation will tip the balance of the overall system (water with wells) in favour of the solid phase. Worse still, this effect becomes more severe the more the simulation is slowed down, since freezing has more time to occur. Yet slowing down the simulation is precisely what we need to do (for reversibility reasons) in order to obtain better accuracy.

We arrive at the somewhat counter-intuitive conclusion that the best approach is a constant volume simulation cell, which encourages coexistence of equal volumes of ice and water, and discourages coexistence of any other ice–water proportion, despite the trickier procedures required for initial calibration in this case.

# CHAPTER V

## SIMULATION – TRUNCATED SYSTEM

The first and simplest application of the method to water was for the TIP4P model with discontinuous truncation.

### 5.1 Simulation Parameters

The geometry and parameters of the TIP4P water model are described in Section 3.1 (page 34). Both Lennard-Jones and electrostatic interactions were truncated (discontinuously) at  $10\text{\AA}$ . As mentioned in Section 2.3.4 (page 15), the cutoff refers to the distance between the centres of mass of two interacting molecules.

We employed molecular dynamics simulation, with the velocity Verlet algorithm, in the  $NVT$  ensemble. The molecules were treated as rigid bodies using the quaternion-based algorithm NO\_SQUISH [18] with 2 fs time step. The temperature was controlled using the Nosé-Hoover method, with translational and rotational motions being controlled by two independent thermostats.

The method was repeated three times, to calculate ice  $I_h$ –water interfacial free energy for each of the crystal orientations described in Section 3.3 (page 35).

For each step, at least 10 trajectories were run. The ice crystal for each trajectory was given its own distinct proton-disordered structure, as described in Section 3.3 (page 35). The ice system contained approx. 2 100 molecules in a simulation cell of dimensions  $L_x \approx 44\text{\AA}$ ,  $L_y \approx 39\text{\AA}$ ,  $L_z \approx 45\text{\AA}$ . The water system with exactly the same  $L_x$  and  $L_y$  dimensions (the cleaving plane is chosen normal to the  $z$ -axis) had approx. 2 400 molecules and  $L_z \approx 42\text{\AA}$ .

## 5.2 Calibration for Coexistence Conditions

The ice  $I_h$  and water densities were calibrated as described in Section 3.4 (page 40). Densities of 938.0 kg/m<sup>3</sup> for ice  $I_h$  and 1010.8 kg/m<sup>3</sup> for water were found to achieve, at 219 K, the approximate ambient pressure of 1 bar.

The ice  $I_h$ –water coexistence temperature was then established as described in Section 3.5 (page 42). Long simulations with a 4 ns timestep of the ice–water interfacial system were run at temperatures 213, 216, 219, 222, 225 K. Melting of the ice–water interfacial system was observed at temperatures above 219 K (see Figure 5.1). The melting temperature of 219 K is lower than for TIP4P models reported in the literature [41, 36, 34, 37], which were in the range 229–232 K. We attribute this to the truncation of the electrostatic interaction at 10 Å, since the higher melting temperature estimates were obtained for the TIP4P model either with full electrostatic interactions (computed via Ewald Sums) [34], or with a larger interaction cutoff of 17 Å [41, 36]. To verify the effect of truncation on the melting temperature, we repeated the coexistence simulations for TIP4P with Ewald Sums, and the system did not melt at 230 K.

Based on this evidence, we conclude that the truncation of electrostatic interactions in TIP4P model leads to the decrease of melting temperature. This decrease might not be noticeable with the 17 Å cutoff due to the relatively low precision of the coexistence simulation method, but it is clearly observed for the 10 Å cutoff. We are confident that our estimate of 219 K is not far from the true melting temperature for this system. In fact, if the temperature at which we performed the cleaving process were below the melting temperature for this system, we would have ended up with an excess amount of ice at the end of the four-step cleaving process, which we did not observe.

## 5.3 Results

The individual work for each of the steps and the interfacial free energies calculated for this model are tabulated in Table 5.1. The lengths of the simulation runs, and numbers of trajectories for each step are shown in Table 5.2.

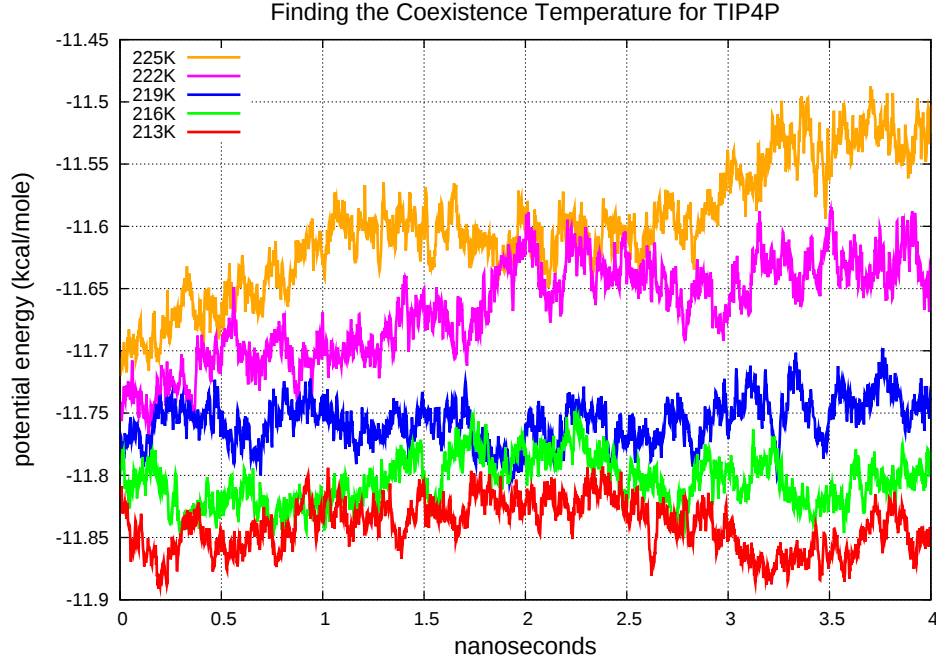


Figure 5.1: A graph illustrating the use of the ‘direct coexistence simulation method’ to determine the melting temperature. Only at the melting temperature is no long-term potential drift observed. The model is TIP4P water with discontinuous truncation at  $10\text{\AA}$ .

|                | Basal       | Prism       | $\{11\bar{2}0\}$ |
|----------------|-------------|-------------|------------------|
| Step 1         | -369.50(5)  | -393.31(10) | -225.26(6)       |
| Step 2, heat   | 1513.00(15) | 1611.14(18) | 1550.22(18)      |
| Step 2, cleave | -312.65(11) | -332.84(17) | -173.7(3)        |
| Step 2, cool   | -1539.2(3)  | -1643.7(9)  | -1572.2(3)       |
| Step 3         | 0.6(6)      | 0.5(3)      | -0.2(6)          |
| Step 4         | 731.06(13)  | 781.80(12)  | 445.9(2)         |
| Total          | 23.3(8)     | 23.6(1.0)   | 24.7(8)          |

Table 5.1: A breakdown of the contributions to  $\gamma_{sl}$  (in  $\text{mJ}/\text{m}^2$ ) for each crystal orientation of truncated TIP4P water

|                | Basal       | Prism       | $\{11\bar{2}0\}$ |
|----------------|-------------|-------------|------------------|
| Step 1         | 0.4 ns (10) | 0.4 ns (5)  | 0.4 ns (10)      |
| Step 2, heat   | 1.0 ns (10) | 0.9 ns (15) | 1.0 ns (10)      |
| Step 2, cleave | 2.4 ns (30) | 1.7 ns (15) | 1.8 ns (20)      |
| Step 2, cool   | 2.6 ns (60) | 4.4 ns (60) | 4.9 ns (40)      |
| Step 3         | 0.8 ns (20) | 1.0 ns (25) | 0.2 ns (5)       |
| Step 4         | 1.3 ns (25) | 1.3 ns (30) | 0.8 ns (20)      |

Table 5.2: A table showing the duration of each step in the simulation runs corresponding to Figure 5.1. The number of trajectories (in each direction) is shown in brackets.

## 5.4 Discussion

### 5.4.1 $\gamma_{sl}$ and its anisotropy

These estimates of  $\gamma_{sl}$  for the ice  $I_h$ –water interfaces are surprisingly close to Hardy’s experimental value of  $29.1 \pm 0.8 \text{ mJ m}^{-2}$  (Section 1.3.1, page 4), considering the approximate nature of the TIP4P model of water. As expected, the value for  $\gamma_{\{11\bar{2}0\}}$  is higher than the values for the other two orientations, which are marginally smaller but very similar.

This similarity in the three values is too close for them to be distinguished at all, within statistical error; we can only conclude that they imply a factor of anisotropy somewhere between 0% and 9%.

A rough theoretical estimate of the anisotropy can be computed, based on the number of broken bonds at the crystal surface [42, 43]. According to this calculation,  $\gamma_{\text{basal}} : \gamma_{\text{prism}} : \gamma_{\{11\bar{2}0\}} \approx 1 : 1.06 : 1.22$ , which represents a significantly greater degree of anisotropy than these computational results indicate.

The anisotropy could also be estimated, in principle, experimentally, from the equilibrium shape of an ice  $I_h$  crystal using the well known Wulff construction [44]. However, to our knowledge, the equilibrium shapes of isolated ice crystals have never been definitively observed [45]. The experimental observation of the oblate ellipsoidal shape of water inclusions in ice  $I_h$  [46] would imply a very large anisotropy with the ratio  $\gamma_{\text{prism}}/\gamma_{\text{basal}} = 1.857$ , but this could also be attributed to the strong influence of mechanical stresses on the shape of the inclusions [47].

In summary, the computational results obtained here seem to indicate that the anisotropy ratios are closer to unity than other estimates have suggested.

### 5.4.2 The Turnbull Coefficient

The Turnbull Coefficient [48],  $C_T$ , is defined by the equation

$$\gamma_{\text{sl}}\rho_{\text{s}}^{-2/3} = C_T\Delta H_{\text{fus}}, \quad (5.1)$$

where  $\rho_{\text{s}}$  is the number density of the solid phase, and  $\Delta H_{\text{fus}}$  is the enthalpy of fusion between the two phases.

$C_T$  commonly takes a value of about 0.45 for metals, and 0.32 for many non-metallic materials. For this model (TIP4P with truncation)  $C_T = 0.45$ , substantially higher than the value for real water,  $C_T = 0.30$ .

The inaccuracy of the model's value of the Turnbull Coefficient can in part be explained by the its underestimation of  $\Delta H_{\text{fus}}$ . For the model,  $\Delta H_{\text{fus}} = 3.18 \text{ kJ mol}^{-1}$ , whilst for real water  $\Delta H_{\text{fus}} = 6.02 \text{ kJ mol}^{-1}$ . This underestimation can in turn be partially explained as the result of truncation of the electrostatic interactions in the model. The TIP4P model with full electrostatic interactions (using Ewald Sums), at its coexistence temperature of 230 K, has a somewhat higher enthalpy of fusion,  $\Delta H_{\text{fus}} = 4.34 \text{ kJ mol}^{-1}$ .

From this reasoning, we conjectured that by repeating the cleaving method to calculate  $\gamma_{\text{sl}}$  for the TIP4P model using Ewald Sums for more accurate calculation of long-range interactions, we would obtain a somewhat higher estimate of  $\gamma_{\text{sl}}$ , closer still to the experimental values mentioned in Section 1.3.1 (page 4). This indeed turned out to be the case, as detailed in the next section, though the excellent agreement obtained in that case must to some extent be fortuitous.

# CHAPTER VI

## SIMULATION – EWALD SUMS

As noted in Section 2.2.3 (page 9), Ewald Sums provide greater accuracy than truncation of electrostatic interactions, and many of the more recent models of water, such as TIP4P-Ew [17], are parametrized for use with Ewald Sums.

The force on a particle is calculated using Ewald Sums as:

$$\begin{aligned} \mathbf{f}_j = & -\frac{q_j}{V_0\epsilon_0} \sum_{\mathbf{k} \neq 0} i\mathbf{k} \exp(\mathbf{k} \cdot \mathbf{r}_j) \frac{\exp(-k^2/4\alpha^2)}{k^2} \sum_n^N q_n \exp(-i\mathbf{k} \cdot \mathbf{r}_n) \\ & + \frac{q_j}{4\pi\epsilon_0} \sum_n^N \frac{q_n}{r_{nj}^3} \left\{ \operatorname{erfc}(\alpha r_{nj}) + \frac{2\alpha r_{nj}}{\sqrt{\pi}} \exp(-\alpha^2 r_{nj}^2) \right\} \mathbf{r}_{nj}. \end{aligned} \quad (6.1)$$

The computational cost of Ewald Sums is significant, particularly for large systems. In the case of the combined ice–water system, consisting of about 4,000 molecules, we observed an increase in computation time by a factor of about 10 compared with smooth truncation at 10Å. The vast majority of this increased computation time is taken by the Fourier space term, which is the first sum in Eq. (6.1).

The performance penalty for using Ewald Sums is particularly acute when applied to the moving wall method, since the essence of this method is to transform separate ice and water systems into a combined system, by transforming the system potential:

$$U(\lambda) = (1 - \lambda)(U_i + U_w) + \lambda U_{iw}, \quad \lambda = 0 \rightarrow 1, \quad (6.2)$$

where  $U_i$  ( $U_w$ ) is the potential of the isolated ice (water) system,  $U_{iw}$  is the potential of the combined interfacial system and  $U$  is the potential of the (non-physical) transformation path between the two. During this transformation, all the molecules

co-exist in two differently-sized simulation cells. Since the Ewald Sum includes interactions not just with nearest neighbour molecules, but also with periodic images, the force between any two particles depends not just on their distance apart, but also on the dimensions of the simulation cell. So the force calculation for all interactions must be repeated twice. By contrast, when truncation is used, such double-calculation of interactions is not required in general, but only for those molecules which are within cutoff range of one of the cleaving planes.

In the face of the daunting computational demands of the Ewald Sum approach, and the limited computer resources available to us, we needed to devise a method for reducing the computation time, described in detail below.

## 6.1 Computation Time for Ewald Sums

Motivated by discussions with Dr Andrei Brukhno of Bradford University, we developed an approach to significantly improve the speed of the method for Ewald Sums. Brukhno had noticed that the contribution to the interaction forces of the Fourier space components of the Ewald Sums was very small compared with that of the real-space terms. Furthermore, as noted above, it is the computation of these components which form the bulk of the computational load. This (initially surprising) observation is perhaps explained by the cancellation of the long-range electrostatic forces in a neutral system without any significant dipole moment.

In order to investigate this further, we ran a series of simulations of an ice-water interfacial system, using the TIP4P-Ew model, but omitting all the Fourier space components of the Ewald Sums. This system can be regarded as a different *model* of water, referred to hereafter as ‘short water’. It should be noted that the idea of using such a potential function is not new: various alternatives to the full Ewald Sums potential were suggested in a paper by Wolf et al. in 1999 [49]. In that paper, the term ‘potential screening’ is used for various alternative potentials, including ‘short water’. We found that there was no significant difference between the observed macroscopic properties of short water, and the full Ewald Sums version; and melting point was indistinguishable at the same density. For example, Figure 6.1 shows a 2 nanosecond equilibration run for the two models at three different temperatures. The comparisons used the coexistence simulation method, described in detail in Section 3.5 (page 42).

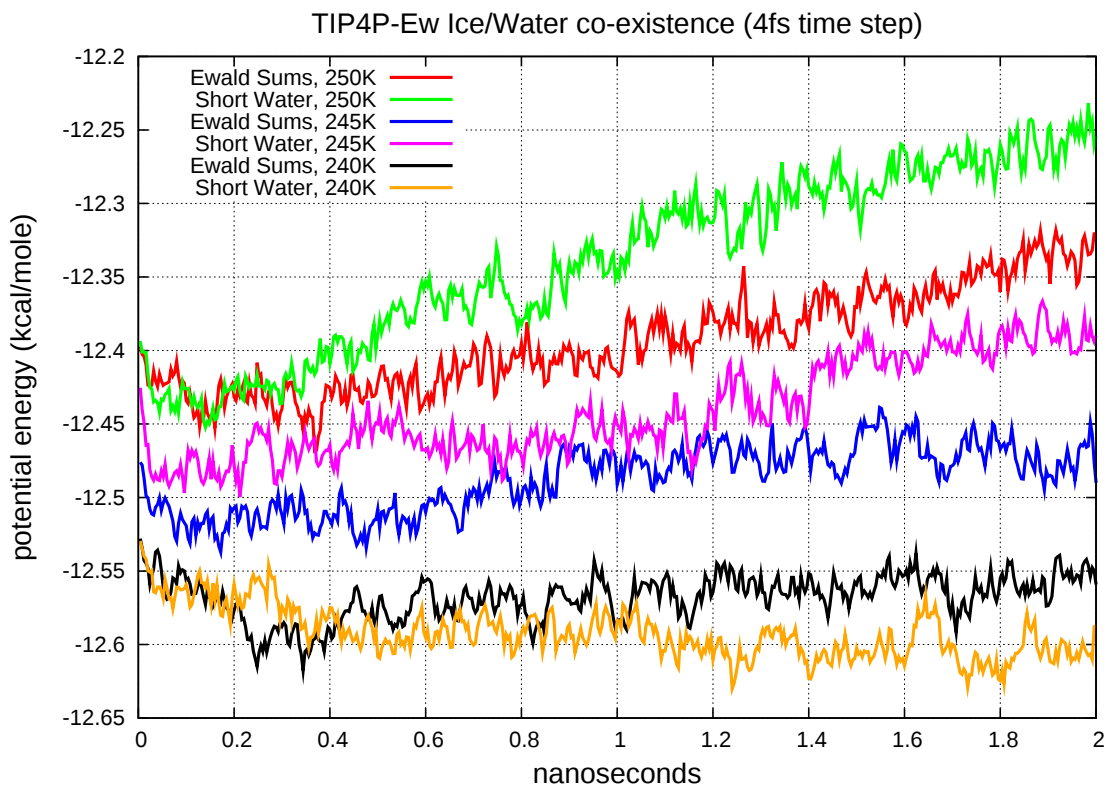


Figure 6.1: A graph illustrating the similarity of Ewald Sums with ‘short water’ for the TIP4P-Ew model. The ‘direct coexistence simulation method’ is used to show the closeness of the two melting temperatures.

Figure 6.1 shows that, although the potential energies of the two models differ somewhat, the melting points are the same to within the accuracy of the timescales of the simulations. The two models exhibit the same melting/freezing behaviour, as indicated by change in potential energy, at the temperatures tested. We also observed close similarity between the two models on both bulk ice and bulk water systems in isolation. Table 6.1 also shows a comparison of potential energy and pressure for pure ice and pure water systems.

These results indicate that a more efficient way of calculating the free energy for systems with Ewald Sums is to transform Ewald Sums ice and water systems into the ‘short water’ (by switching off the reciprocal space part), and then perform the cleaving process on the short water system. It takes a relatively small amount of computing time to reversibly transform one model to the other. In particular, the following approach can be adopted:

| Model    | Potential   | Phase | Pressure, atm | Potential, kcal/mole |
|----------|-------------|-------|---------------|----------------------|
| TIP4P    | Ewald Sums  | Ice   | -34(1)        | -12.0118(5)          |
| TIP4P    | Short Water | Ice   | 9(3)          | -12.0087(6)          |
| TIP4P    | Ewald Sums  | Water | 19(10)        | -10.980(3)           |
| TIP4P    | Short Water | Water | 19(22)        | -10.963(5)           |
| TIP4P-Ew | Ewald Sums  | Ice   | 102(3)        | -13.0489(5)          |
| TIP4P-Ew | Short Water | Ice   | 149(2)        | -13.0455(6)          |
| TIP4P-Ew | Ewald Sums  | Water | 25(11)        | -11.966(2)           |
| TIP4P-Ew | Short Water | Water | 29(24)        | -11.949(5)           |

Table 6.1: A table comparing Ewald Sums with ‘short water’. Pressure and potential energy are shown for the different phases and crystal orientations.

1. Before starting step 1 of the cleaving method, transform the equilibrated ice to the short water model by smoothly switching off the Fourier space components of the Ewald Sum.
2. Perform a similar transformation to short water for the equilibrated water system before starting step 2.
3. Perform the original steps (1 - 4) of the cleaving method using the short water model.
4. Finally, transform the resulting equilibrated (short water) ice–water interfacial system back to full Ewald Sums by smoothly switching the Fourier space components back on.

Considering all these steps as a single enhanced method, it remains a method for creating an interface of full Ewald Sums water. Providing all the steps are reversible, the free energy between the end-points is calculated. Both end-points are the full Ewald Sums model, so it is the free energy of that model which is calculated, regardless of the fact that during most of the transformation path, the original cleaving method is performed on a somewhat different model.

The transformations between full Ewald Sums and short water and back again can be regarded as introduction of an ‘external potential’, and they can be accomplished using the standard non-equilibrium methods for any such transformation, as described in detail above for the original cleaving method steps.

This approach does not in fact require that the two models share the same co-existence characteristics. Switching to any different model will work in principle:

providing any necessary additional steps are included to keep the system at co-existence (for example by changing the temperature while the model is changed) the overall path will still be reversible. However, the modification to the method is particularly straightforward in the case of short water, since the co-existence conditions coincide with the Ewald Sums model. It should further be noted that the characteristics are not almost identical in general, only in certain circumstances, including those presently under consideration, namely pure neutral water, pure proton-disordered hexagonal ice and interactions between the two.

Since short water is so much cheaper computationally than full Ewald Sums, the approach outlined above gives significant savings; all of the time-consuming steps of the cleaving method are performed on short water. Some trial runs confirmed that the transformation to short water and back again is straightforward, and does not suffer from hysteresis.

Graphs illustrating the switch from Ewald Sums to ‘short water’ for equilibrated ice are shown in figures 6.2, 6.3, and 6.4. Each trajectory is in effect a switch between the two water models. A full explanation of the graphs and their interpretation is given in Section 4.6, where similar graphs were introduced for step 2.

The same graphs for the equilibrated water system are shown in figures 6.5, 6.6, and 6.7, and for the combined interface system in figures 6.8, 6.9, and 6.10.

Since the transformation between Ewald Sums and short water is straightforward, the additional computation time required for the transformation is negligible compared to the time saved in the rest of the process. Overall, we obtained a speed-up by a factor of about 7, taking account of the extra steps in transforming between the two models.

All of the Ewald Sums results reported here were obtained using this approach.

## 6.2 Methodology

Calculations were performed on two models: TIP4P and TIP4P-Ew. The geometry and parameters of these models are described in Section 3.2 (page 35) and Section 3.1 (page 34). Molecular forces were calculated using Ewald Sums, with real-space cutoff at  $8.5\text{\AA}$ , and parameters  $\alpha = 0.26/\text{\AA}$  and  $k = 1.15/\text{\AA}$ .

The method was repeated three times, to calculate ice  $I_h$ –water interfacial free energy for the  $\{0001\}$  (basal),  $\{1\bar{1}00\}$  (prism), and  $\{11\bar{2}0\}$  interfaces.

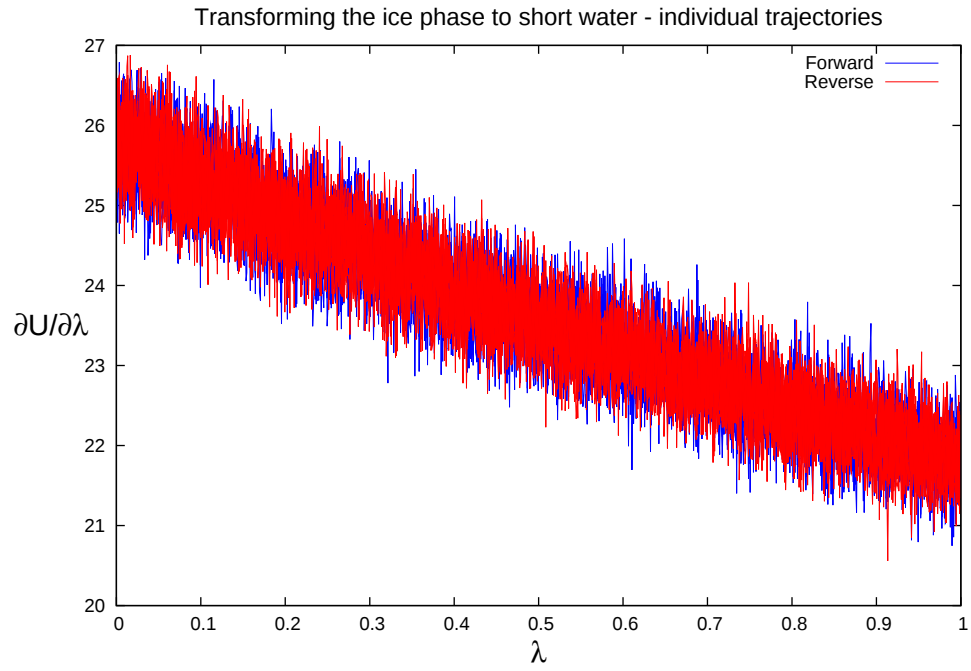


Figure 6.2: Isolated ice system: individual ‘trajectory work’ paths for the ‘short water’ switch.

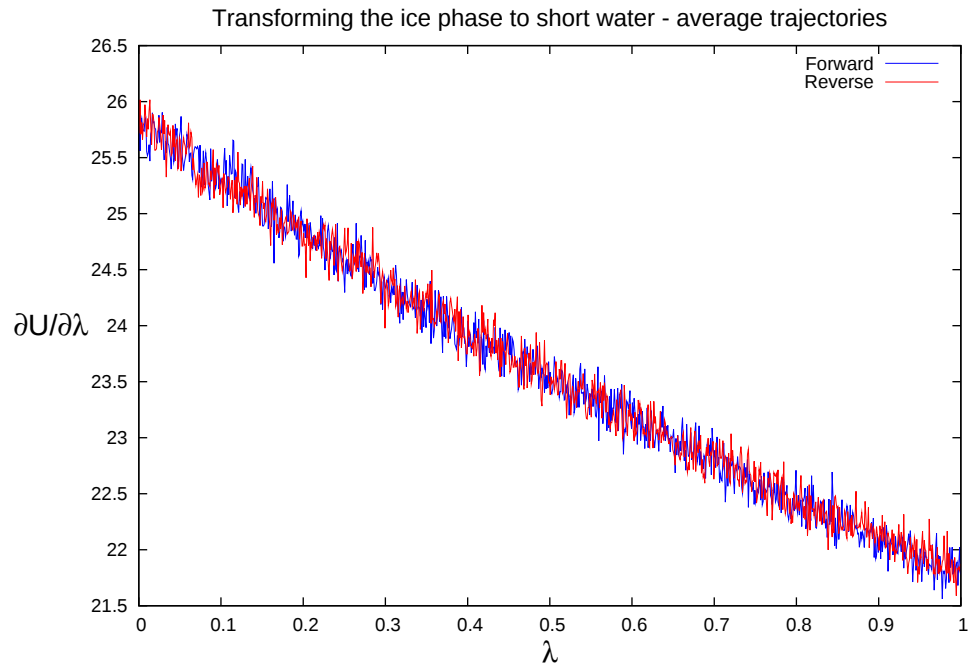


Figure 6.3: Average paths for the trajectories shown in Figure 6.2

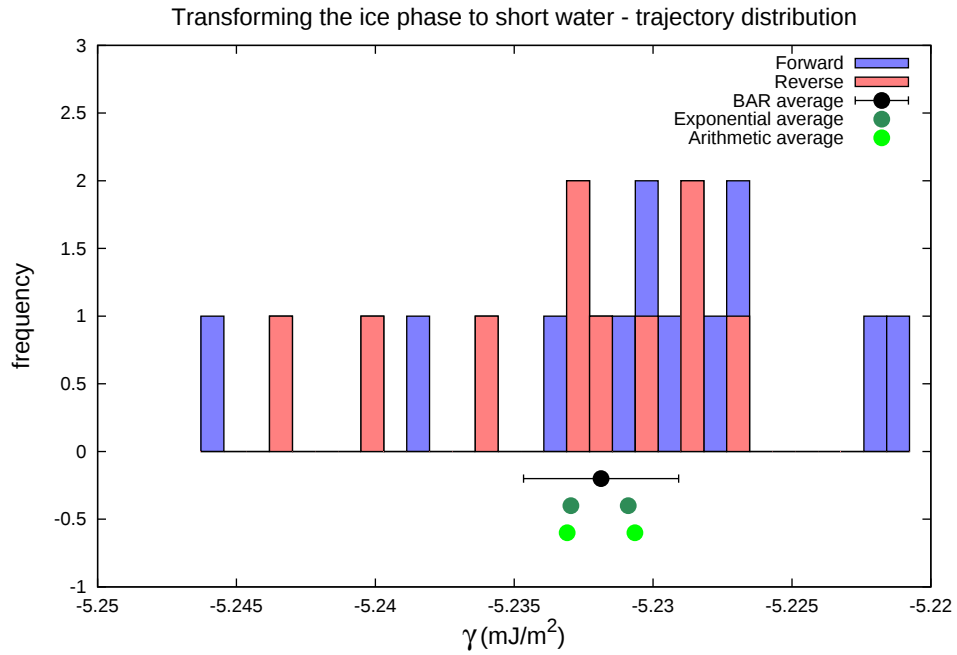


Figure 6.4: Distribution of ‘trajectory work’ for the trajectories shown in Figure 6.2

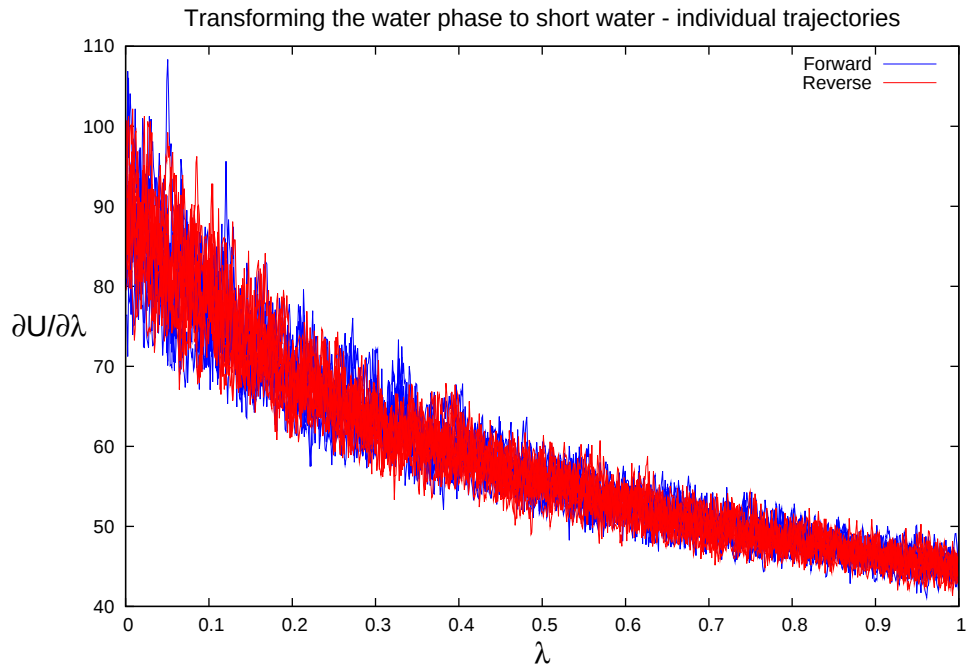


Figure 6.5: Isolated water system: individual ‘trajectory work’ paths for the ‘short water’ switch.

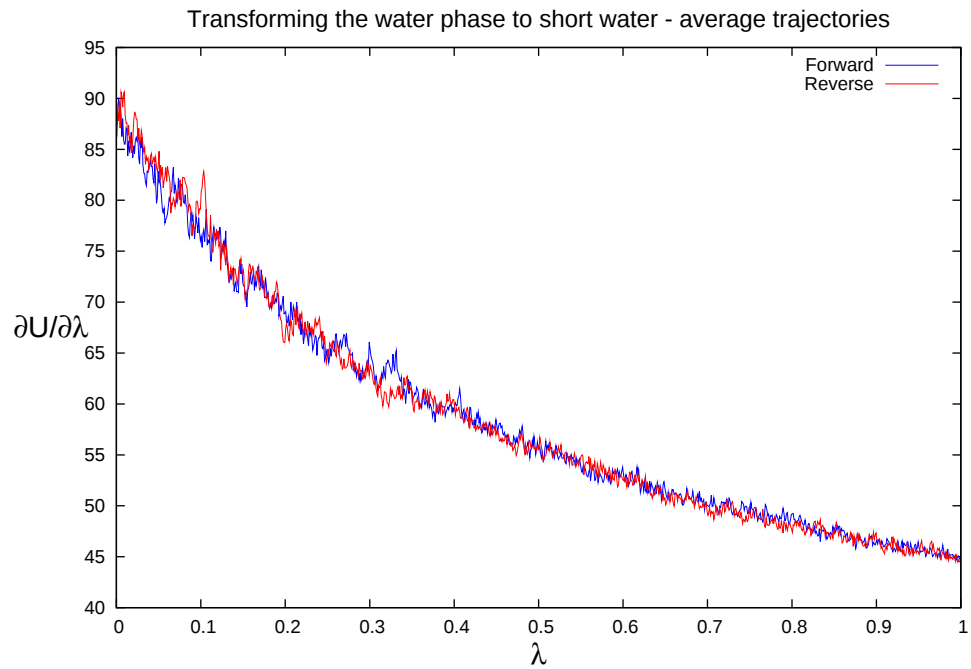


Figure 6.6: Average paths for the trajectories shown in Figure 6.5

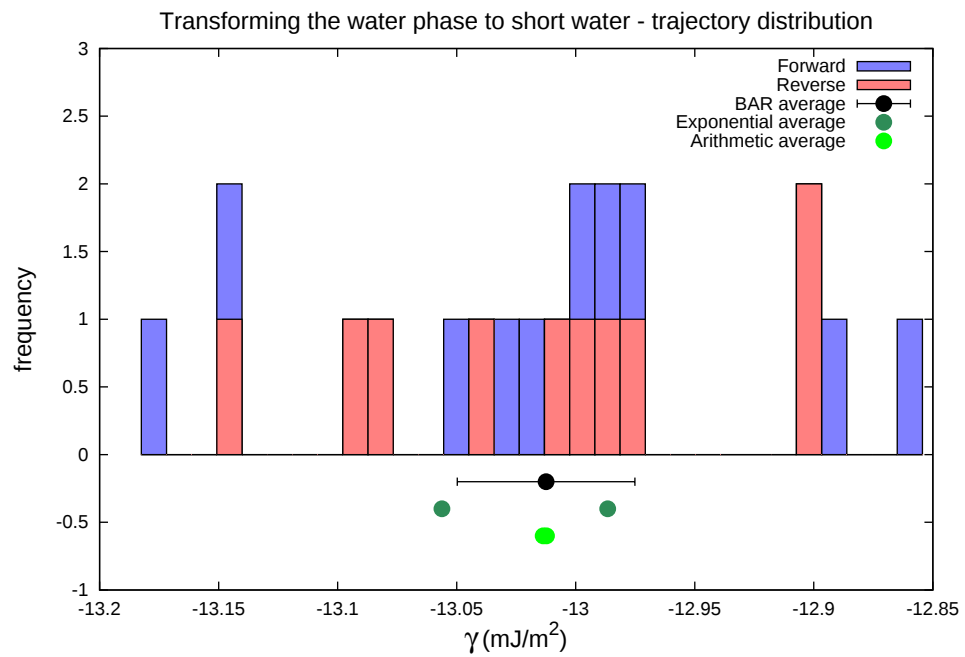


Figure 6.7: Distribution of ‘trajectory work’ for the trajectories shown in Figure 6.5

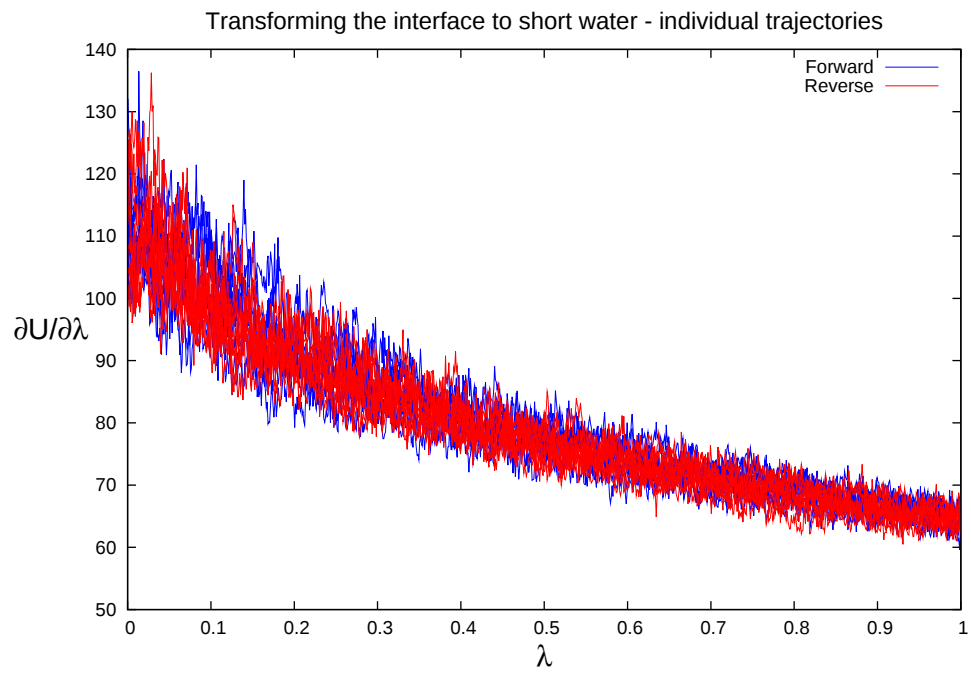


Figure 6.8: Combined ice–water system: individual ‘trajectory work’ paths for the ‘short water’ switch.

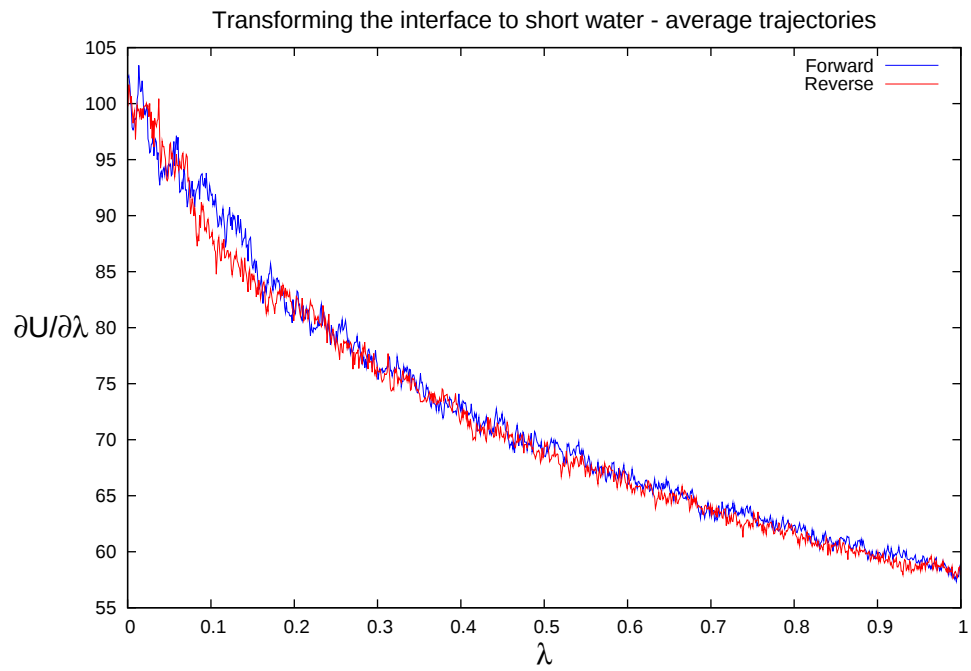


Figure 6.9: Average paths for the trajectories shown in Figure 6.8

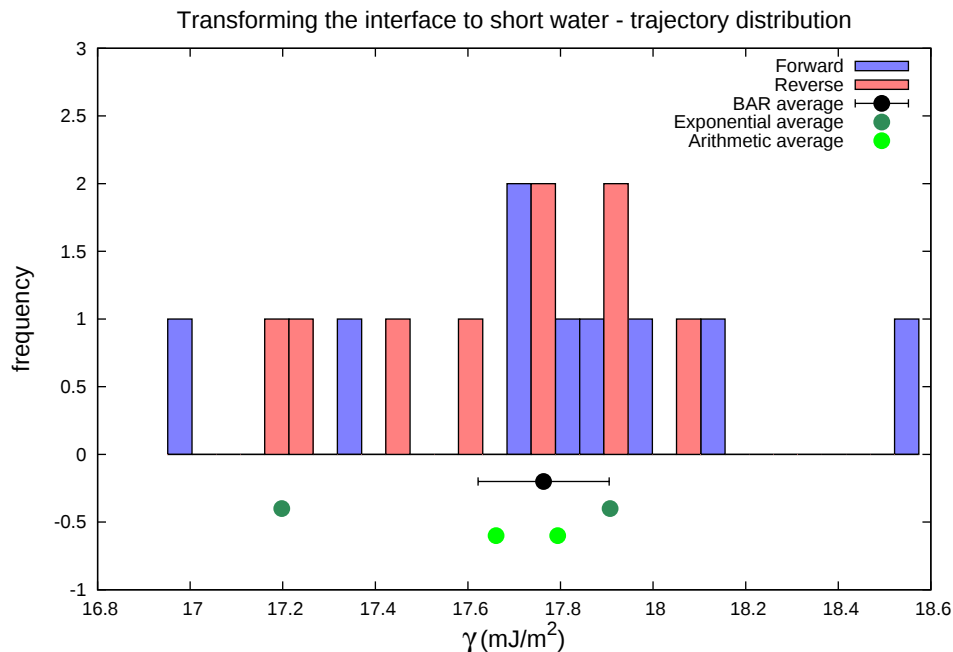


Figure 6.10: Distribution of ‘trajectory work’ for the trajectories shown in Figure 6.8

We employed molecular dynamics simulation, with the velocity Verlet algorithm, in the  $NVT$  ensemble. The molecules were treated as rigid bodies using the quaternion-based algorithm NO-SQUISH [18] with 4 fs time step. The temperature was controlled using a newly-developed Langevin thermostat, described in detail in Chapter 2.5.5 (page 27), with thermostatic control over both translational and rotational motion (the new mathematical development was for stochastic thermostatic control over the rigid body rotations).

For each step, 10 trajectories in each direction were run. The ice crystal for each trajectory was given its own distinct proton-disordered structure, as described in Section 3.3 (page 35). The ice system contained approx. 2100 molecules in a simulation cell of dimensions  $L_x \approx 44\text{\AA}$ ,  $L_y \approx 39\text{\AA}$ ,  $L_z \approx 45\text{\AA}$ . The water system with exactly the same  $L_x$  and  $L_y$  dimensions (the cleaving plane is chosen normal to the  $z$ -axis) had approx. 2400 molecules and  $L_z \approx 42\text{\AA}$ .

The ice  $I_h$  and water densities were calibrated as described in Section 3.4 (page 40). The ice  $I_h$ –water coexistence temperature was then established as described in Section 3.5 (page 42). The densities and temperatures for the two models are summarised in Table 6.2.

| Model    | Phase | Density                | Temperature |
|----------|-------|------------------------|-------------|
| TIP4P    | Ice   | 938 kg/m <sup>3</sup>  | 230K        |
| TIP4P    | Water | 1000 kg/m <sup>3</sup> | 230K        |
| TIP4P-Ew | Ice   | 935 kg/m <sup>3</sup>  | 245K        |
| TIP4P-Ew | Water | 992 kg/m <sup>3</sup>  | 245K        |

Table 6.2: A table showing coexistence densities and Temperatures for TIP4P and TIP4P-Ew water with Ewald Sums

## 6.3 Results

The results, including the work for each step are tabulated in tables 6.4 and 6.5. Some additional steps have been introduced to the original method, as used for the truncated system and described in detail in Section 4.2 (page 45). These additional steps, explained in detail in Section 6.1 (page 72), are summarised below:

1. Step Pre-1: Switch equilibrated ice to the short water model before starting step 1.
2. Step Pre-2: Switch equilibrated water to the short water model before starting step 2.
3. Step 2: The third stage now increases the water potential from 70% to 85% instead of 100%.
4. Step 3: is now performed with the water potential (constantly) at 85%.
5. Step 4a: Restore the water potential from 85% to 100%, while simultaneously reducing the wells to 25% strength.
6. Step 4b: Remove the remaining 25% of the well strength (forward direction only).
7. Step Post-4: Switch the equilibrated combined system to full Ewald Sums.

## 6.4 Discussion

### 6.4.1 Turnbull Coefficients

The Turnbull coefficients [48],  $C_T$  corresponding to each  $\gamma_{sl}$  are shown in Table 6.6

|             | Basal      | Prism      | $\{11\bar{2}0\}$ |
|-------------|------------|------------|------------------|
| Step Pre-1  | -5.232(3)  | -5.565(2)  | -5.343(1)        |
| Step 1      | -368.75(3) | -391.46(4) | -452.13(4)       |
| Step Pre-2  | -13.01(4)  | -13.81(4)  | -13.32(4)        |
| Step 2      | 440.4(3)   | 467.9(3)   | 381.3(5)         |
| Step 3      | -50.8(1)   | -39.4(2)   | -25.24(7)        |
| Step 4a     | -166.3(3)  | -192.1(4)  | -87.4(2)         |
| Step 4b     | 170.4(3)   | 182.9(4)   | 211.3(2)         |
| Step Post-4 | 17.8(1)    | 19.1(1)    | 18.3(1)          |
| Total       | 24.5(6)    | 27.6(7)    | 27.5(7)          |

Table 6.3:  $\gamma_{sl}$  (in mJ/m<sup>2</sup>) for TIP4P water using Ewald SumsTable 6.4: A breakdown of the contributions to  $\gamma_{sl}$  (in mJ/m<sup>2</sup>) TIP4P water with Ewald Sums

|             | Basal      | Prism      | $\{11\bar{2}0\}$ |
|-------------|------------|------------|------------------|
| Step Pre-1  | -5.773(3)  | -6.146(4)  | -5.897(3)        |
| Step 1      | -367.16(4) | -389.77(5) | -450.20(5)       |
| Step Pre-2  | -13.98(6)  | -14.84(6)  | -14.28(6)        |
| Step 2      | 512.0(4)   | 544.1(4)   | 455.0(5)         |
| Step 3      | -54.58(8)  | -42.1(3)   | -27.1(1)         |
| Step 4a     | -233.1(4)  | -264.4(4)  | -157.4(2)        |
| Step 4b     | 168.6(4)   | 181.2(4)   | 210.0(3)         |
| Step Post-4 | 19.5(2)    | 20.9(2)    | 18.2(1)          |
| Total       | 25.5(7)    | 28.9(8)    | 28.3(7)          |

Table 6.5: A breakdown of the contributions to  $\gamma_{sl}$  (in mJ/m<sup>2</sup>) TIP4P-Ew water with Ewald Sums

| Model    | Orientation      | Turnbull Coefficient |
|----------|------------------|----------------------|
| TIP4P    | Basal            | 0.347                |
| TIP4P    | Prism            | 0.391                |
| TIP4P    | $\{11\bar{2}0\}$ | 0.389                |
| TIP4P-Ew | Basal            | 0.342                |
| TIP4P-Ew | Prism            | 0.387                |
| TIP4P-Ew | $\{11\bar{2}0\}$ | 0.379                |

Table 6.6: Turnbull Coefficients for Ewald Sums Models

As discussed in Section 5.4.2 (page 70), the Turnbull coefficient of the truncated model, 0.45, overestimates the real water value of 0.30. This is related to the model’s underestimation of enthalpy of fusion. For real water,  $\Delta H_{\text{fus}} = 6.02$  kJ/mol, compared with 3.18 kJ/mol for TIP4P with truncation. For the same model with Ewald Sums,  $\Delta H_{\text{fus}} = 4.34$  kJ/mol, and for TIP4P-Ew with Ewald Sums,  $\Delta H_{\text{fus}} = 4.53$  kJ/mol, both significantly closer to the value for real water. As can be seen from the table, the values of  $C_T$  for the Ewald Sums models are also closer to, though still an overestimate of, the real water value of 0.30. Despite the truncated potential’s failure to reproduce a reasonable value for  $\Delta H_{\text{fus}}$ , it still provides an estimate of interfacial free energy surprisingly close to the Ewald Sums models.

The values of both the Turnbull Coefficient and enthalpy of fusion seem to be more sensitive to changes in the model than the value of  $\gamma_{\text{sl}}$ .

Our estimate for  $\gamma_{\text{sl}}$  for the TIP4P model with truncation is close to, though somewhat lower than the previously published experimental results mentioned in Section 1.3.1 (page 4), and the introduction of Ewald Sums brings the estimate even closer.

### 6.4.2 $\gamma_{\text{sl}}$ for Short Water

The values of  $\gamma_{\text{sl}}$  for the short water model can be calculated from the above results by omitting the transformation steps ‘Pre-1’, ‘Pre-2’ and ‘Post-4’ (as described in Section 6.3, page 81) from the sum. The results are shown in Table 6.7, alongside the Ewald Sum figures for comparison. The comparison confirms that the short water model provides a good approximation to models with full electrostatic interactions, as far as interfacial free energy is concerned. The figures are indistinguishable (within the statistical error) in 5 out of the 6 cases. There is a significantly larger difference

| Model    | Orientation      | Ewald Sums | Short Water |
|----------|------------------|------------|-------------|
| TIP4P    | Basal            | 24.5(6)    | 25.0(6)     |
|          | Prism            | 27.6(7)    | 27.9(7)     |
|          | $\{11\bar{2}0\}$ | 27.5(7)    | 27.8(7)     |
| TIP4P-Ew | Basal            | 25.5(7)    | 25.8(7)     |
|          | Prism            | 28.9(8)    | 29.0(7)     |
|          | $\{11\bar{2}0\}$ | 28.3(7)    | 30.3(7)     |

Table 6.7: Comparison of  $\gamma_{sl}$  (in mJ/m<sup>2</sup>) between Ewald Sums and ‘short water’

in the case of the  $\{11\bar{2}0\}$  orientation for the TIP4P-Ew model. This discrepancy is somewhat surprising given the closeness of the other figures, although even in this worst case, the figures are within 7% of each other.

## 6.5 Conclusions

The approach of switching to the ‘short water’ model seems very effective; it reduces computation time significantly, and the additional contribution to the overall error bars is negligible.

The results for the TIP4P model with Ewald Sums compare well with the same model using truncation. The values for  $\gamma$  are slightly higher which seems reasonable considering the somewhat higher melting temperature of the model when using Ewald Sums. Comparing the two Ewald Sums results, the values for TIP4P-Ew are somewhat higher again (consistently for each crystal orientation) than for TIP4P, which again seems reasonable given the higher melting temperature of the TIP4P-Ew model.

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