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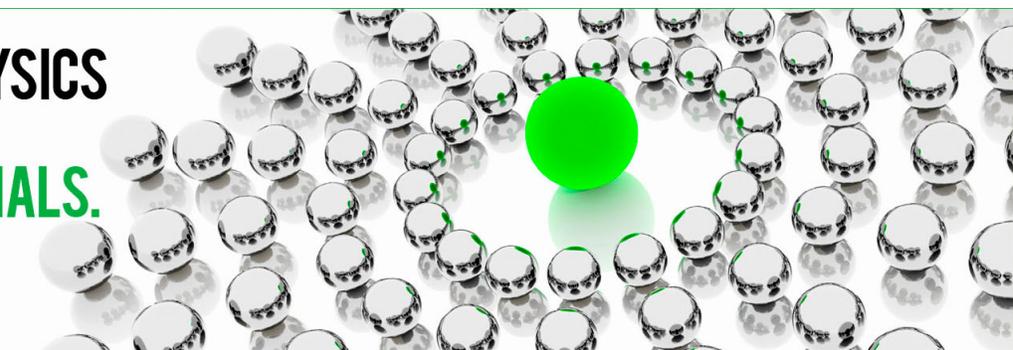
A simple approximation for forces exerted on an AFM tip in liquid

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The critical quantity in understanding imaging using an atomic force microscope is the force the sample exerts on the tip. We put forward a simple one-to-one force to water density relationship, explain exactly how it occurs, and in which circumstances it holds. We argue that two wide classes of atomic force microscope (AFM) tip should lead to at least qualitative agreement with our model and represent a significant fraction of AFM tips as currently prepared. This connection between the short-range force and the unperturbed equilibrium water density removes the need to perform simulations for each tip location, conservatively speeding up simulations by around three orders of magnitude compared to current methods that explicitly calculate the force on a tip model at each point in space. © *2013 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4800770]

I. INTRODUCTION

The ability to quantitatively measure 3D water structure would provide a significant new tool for understanding solvated interfaces, where water layers, and especially closely bound molecules, have important roles in biological activity, catalysis, crystal growth or dissolution, and colloid aggregation.[1–5] Furthermore, the overall structuring of liquid above interfaces has been implicated in long-range interactions between surfaces,[6,7] as well as conductivity, viscosity, and transport in nanofluids.[8,9]

Techniques to quantitatively probe water structure to date have some limitations; X-ray measurements detect the laterally averaged electron density above a surface,[10,11] whilst the surface force apparatus (SFA) can provide detailed information on the average force between two surfaces[6,12] as a function of distance. In principle, the atomic force microscope (AFM) should be able to provide additional, laterally resolved, data beyond that achievable by X-ray or SFA measurements, making possible the examination of spatial correlations at surfaces. However, exactly what the non-contact AFM (nc-AFM) measures, and how invasive the measurement is, is still open to debate.[13]

The main quantity of interest for understanding atomic scale resolution in liquid nc-AFM measurements is the variation in the force between the tip apex and the surface. Longer ranged macroscopic forces also exist, but they can be included using analytical models or, as they are not site specific, empirically removed from experimental data. Over almost two decades cluster models of the tip apex have been developed and compared to experimental measurements in ultra high vacuum, in several cases leading to quantitative agreement between theory and experiment.[14] Recently, we took tip models similar to Ref. 14 as the starting point for our investigations into the contrast mechanism in solution and calculated the

free energy change as the tip approached the surface in a fully solvated cell.[15–17] Calculations based upon integral-equation methods have also been employed.[18] Whilst these approaches led to forces of the correct magnitude to explain the origin of atomic contrast, the calculations are somewhat cumbersome and expensive. This drives our effort to develop good approximations that allow quicker simulation of nc-AFM imaging. A cartoon showing the successive levels of approximation we will describe in detail below is shown in Figure 1. The use of the cluster models described above corresponds to moving from the full macroscopic model, Fig. 1(a), to the atomistic tip model shown in Fig. 1(b).

Recent observations show that experimental force curves measured by nc-AFM[19,20] do show features that can be correlated with those measured by X-ray reflection[21,22] experiments. This implies a direct correlation between the unperturbed water density above a sample and the force measured by a nc-AFM may be expected. It has also been observed that whilst quantitative differences exist in measurements above well prepared surfaces, qualitatively measurements using different cantilevers and taken at different times are often in good agreement,[13] suggesting that there may be common features to many solvated AFM tips that lead to well defined classes of contrast.

II. MODEL

Two classes of tip that might exist fairly universally in aqueous solution are:

- sharp hydroxylated tips – for instance an isolated silanol (Si–OH) group on the end of an ultrasharp silicon or silicon nitride tip that has been partly oxidised.
- tightly bound water molecules – if a tip is terminated by an ionic material with significantly charged cations (e.g., Si–OH$_2$ or Ca–OH$_2$ in tips terminated with silica or fluorite clusters), it is expected that water molecules

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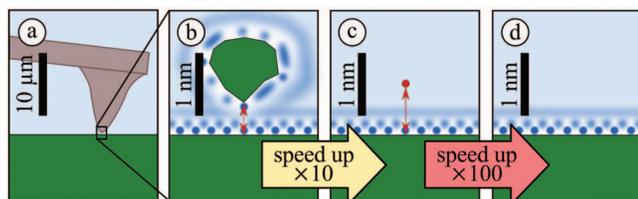
FIG. 1. Simplifying the model system, reducing the computational effort by several orders of magnitude: (a) The actual experimental setup, inaccessible to atomistic simulations; (b) free energy calculations with a fully solvated nanocluster tip; (c) free energy calculations with a single water molecule as tip model; (d) local water density calculation from equilibrium simulations.

will adsorb quite strongly. On a time average they will be present during the imaging process between the *actual tip* and surface. In this case any closely bound water layer is actually part of the tip.

Molecular dynamics simulations of solvated nanoclusters of fluorite[15, 16] and silica[23] show that these functional groups are common and are present for large percentages of the simulation time; by this we mean that even though the residence time of a water molecule above a given cation site is only ~0.25 ns,[16] as soon as it leaves, another water molecule will take its place, reforming the tip model. Particular examples taken from molecular dynamics simulations illustrating both of the classes of tip terminations are shown in Figure 2.

The surface force apparatus community has long put forward the idea that the force measured between two parallel plates is directly related to the water density at the surface (contact value theorem).[12] The AFM uses a rather different experimental setup and geometry compared to SFA. In a paper measuring force-distance curves above an Al_2O_3 surface using nc-AFM,[20] it was proposed that a similar force vs. water-density relationship would hold. However, the authors note that the relationship is unlikely to hold reliably in practice, and the circumstances when it might be valid are not well defined.

In this article we put forward a simple one-to-one force to water-density relationship, explain exactly how it occurs, and in which circumstances it holds. We suggest that the two wide classes of AFM tip proposed above should lead to at least qualitative agreement with our model. As we can connect the short-range force to the unperturbed equilibrium water density, we do not have to perform the calculations at each tip location, and, therefore, simulations will be at least three orders of magnitude faster than current methods that explicitly calculate the force on a tip model at each point in space. We note that calculating the water density over moderately complicated surfaces will soon be within reach of first principles based molecular dynamics.

From the arguments developed above based on the observation of molecular dynamics trajectories of tips in water and the likelihood of common types of tip termination, we take a single water molecule as the tip model and calculate the change in free energy as it approaches the surface over different lateral positions, Figure 1(c). For the explicit free energy calculations we use free energy perturbation (FEP) theory[24] in exactly the same way as in our previous simulations of the force on a nc-AFM tip,[16] but using a water molecule as a tip. The calculations are readily performed, converging much more rapidly than when a larger nanocluster is used to represent the AFM tip.

In Figure 3 we present the local density of water molecules at the interface with the (111) surface of fluorite obtained from equilibrium molecular dynamics simulations. In the following, we will show that the cost in free energy to bring a water molecule from bulk to a particular position **r** close to the surface is directly related to the deviation of the local water density $\rho(\mathbf{r})$ from the bulk value ρ_0,

$$\Delta F(\mathbf{r}) = -k_{\mathrm{B}} T \ln(\rho(\mathbf{r})/\rho_0). \tag{1}$$

The Helmholtz free energy of the system is

$$F(N, V, T) = -k_{\mathrm{B}} T \ln Q = -k_{\mathrm{B}} T \ln Z_N + \mathrm{const}, \tag{2}$$
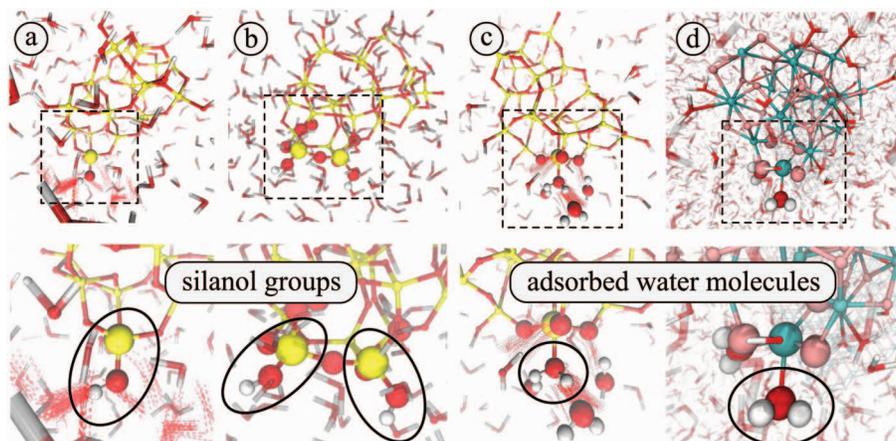
FIG. 2. Tip models extracted from molecular dynamics simulations that expose a flexible OH group to the environment. Bulk solvent molecules are shown as transparent "v" shapes with O red and H white. Atoms shown as larger balls are the tip terminus and its local environment. Silicon is yellow, oxygen is red, calcium is turquoise, and fluorine is pink. Upper figures show overall views of the nanoclusters, lower figures zoom in on the area of interest. (a) Silanol group –Si–OH on a silica cluster; (b) two neighbouring (vicinal) silanol groups on a silica cluster (geminal $Si(OH)_2$ groups are also possible); (c) water molecule adsorbed on a silica cluster; (d) water molecule adsorbed on a CaF_2 cluster.
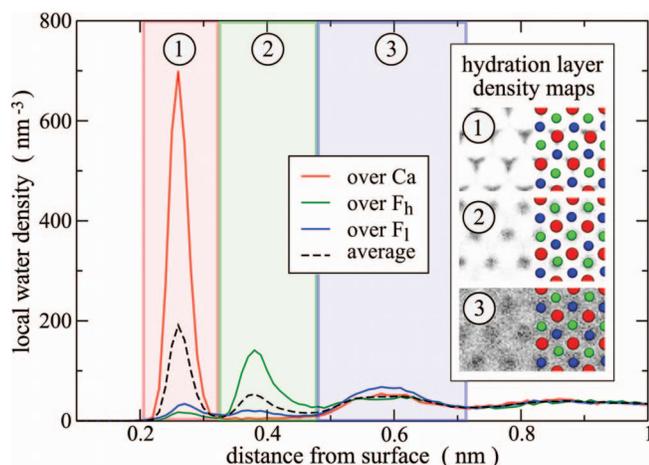
FIG. 3. The local water density at the fluorite (111)/water interface. The local water density $\rho(\mathbf{r})$ is the time average of counts of water molecules within a $0.1 \times 0.1 \times 0.1$ nm^3 cube centered at position $\mathbf{r}$. The red, green, and blue curves indicate the local water densities over the calcium (Ca), protruding fluorine (Fh), and sub-surface fluorine (Fl) sites, respectively. The dashed black curve shows the laterally averaged water density. The inset shows that the areas of high water density (dark) within the first (1), second (2), and third (3) hydration layer, match the sub-lattices of Ca (red), Fh (green), and Fl (blue) in the surface.

where Q is the partition function, and Z_N is the configurational part of the partition function,

$$Z_N = \int d\mathbf{r}^N \exp(-\mathcal{V}(\mathbf{r}^N)/k_B T). \qquad (3)$$

We can define a constrained configurational partition function, considering only systems where one water molecule is located at position $\mathbf{r}$,

$$Z(\mathbf{r}) = \int d\mathbf{r}^N \delta(\mathbf{r}_1 - \mathbf{r}) \exp(-\mathcal{V}(\mathbf{r}^N)/k_B T). \qquad (4)$$

The free energy difference for a water molecule to move from bulk to a certain position $\mathbf{r}$ is

$$\Delta F(\mathbf{r}) = -k_B T \ln(Z(\mathbf{r})/Z_N). \qquad (5)$$

The time-averaged ratio $\rho(\mathbf{r})/\rho_0$ observed in a MD simulation corresponds to the ratio of the constrained and full configurational partition functions,

$$\frac{\rho(\mathbf{r})}{\rho_0} = \frac{Z(\mathbf{r})}{Z_N}, \qquad (6)$$

and we recover Eq. (1). The force on the AFM tip is then given by the derivative of the free energy with respect to the tip-surface distance,

$$f(z) = -\frac{dF(z)}{dz} = \frac{k_B T}{\rho(z)} \frac{d\rho(z)}{dz}. \qquad (7)$$

Figure 4 illustrates this relation by comparing the free energies calculated using FEP on a water model tip (Fig. 1(c)) or using Eq. (1) (Fig. 1(d)). The curves obtained by the FEP calculation of the water model tip, and those obtained directly from the unperturbed water density are in excellent agreement. We note that the method proposed here is close to being a simulation counterpart to the experimental method of
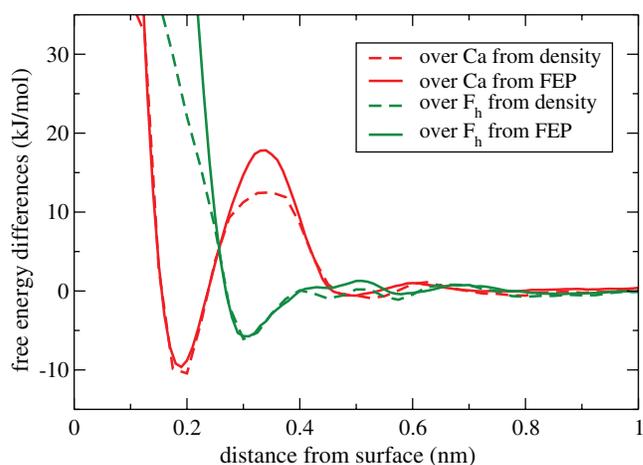
FIG. 4. Comparison of the free energy curves for water molecules above CaF$_2$ with those obtained from the water density using Eq. (1). Density-derived curves are dashed, and those from free energy perturbation calculations are shown as solid curves.

Cleveland *et al.* for the reconstruction of hydration forces in contact mode AFM.[25]

We have further tested our model by comparing the free energy curves obtained from Eq. (1) with the free energy profiles obtained from FEP calculations with a sharp CaF$_2$ nanocluster tip model,[15, 16] as depicted in Figure 2(d). The free energy curves obtained with both methods, over the three different surface sites of fluorite (111) are shown in Figure 5. Over the Ca cation site, where water molecules in the first hydration layer exhibit the strongest spatial ordering (see Figure 3), the agreement with the simple model is excellent: the positions of extrema in the free energy profiles match, and the changes in free energy are of the same order of magnitude. This confirms that the sharp AFM tip is strongly interacting with a single hydration layer water molecule directly above the fluorite surface. Over the two fluorine anion sites, where the hydration layers exhibit less lateral order, the agreement between the simple tip model and the full cluster tip simulation is not as strong. In particular, we think that collective
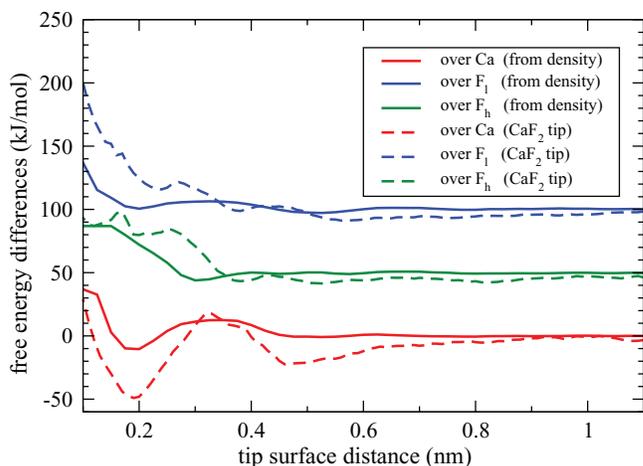
FIG. 5. Comparison of the simple model and simulations with an explicit nanocluster tip: Free energy curves over Ca (red), Fh (green), and Fl sites (blue) in a fluorite surface. Curves obtained from the local water density are solid, curves obtained from FEP with a sharp CaF$_2$ nanocluster tip are dashed.

relaxation of the tip, which leads to uncertainty in the apparent tip height when comparing the full curves to our model, and direct tip-surface interactions are more important in cases with less defined water structure. Nonetheless, we think the general agreement is encouraging and that this model is suitable for rapidly generating approximate force maps over complex surfaces, for example, for use in optimizing AFM setups via simulated instrumentation as well as interpretation of experimental images.

III. DISCUSSION

The data presented above confirm that if the tip apex behaves like a single water molecule, we can make a simple and direct connection between the local water density and the free energy change due to tip approach:

- for nc-AFM tips that can be approximated as water molecules, the measured force is a simple function of the *local water density*.
- if we can calculate, or measure by other methods, the water density, we can investigate how closely a given experimental tip is approximated by our tip model.
- it is possible to simulate nc-AFM *force spectroscopy* from only equilibrium properties of the unperturbed system, but only where the tip falls into one of the two classes listed – hydroxylated tip and tip with closely bound water.

The significance of the first point is that it should be possible to very closely link force measurements to the equilibrium, undisturbed water structure. Combined with points two and three, this could provide a significant boost in the understanding of water structuring at interfaces. It also implies that hydroxylated tips and tip apexes with closely bound water molecules are not invasive and come closest to directly measuring the unperturbed water density above a surface. Indeed, it should be possible to convert force spectroscopy data directly into water density. Conversely, it is possible to take the natural logarithm of water density on a grid obtained from simulation to obtain the short range force "spectrum" measured by nc-AFM. On well characterised samples, it should be possible to see how well the actual tip corresponds to this idealised situation by comparing the measured force to theory or other experimental measurements (e.g., X-ray or SFA). In our hypothetical ideal nc-AFM measurement, it is the water density that is directly probed – not the surface.

IV. RELATING THE MODEL TO EXPERIMENT

The model may be applicable in the following experimental conditions:

- the hydration layers are strongly structured, such as over a surface with periodic positive and negative charges (e.g., ionic or organic crystal surfaces,[19,26,27] self-assembled monolayer of organic molecules with varying functional group terminations,[13] or lipid bilayers[28]). The stronger the variations in water density $\rho(\mathbf{r})$, the better the agreement with the simple model should be.

- the liquid is either pure water, or a very dilute solution, to reduce the effect of additional atomic-scale interactions between the tip and ions close to the surface.[29] In principle, the model should hold for any simple solvent consisting of small, polar molecules.
- the sharp tip is oscillating within the hydration layers, oscillation amplitudes are small compared to the diameter of a liquid molecule, and the tip does not come in contact with the surface. These are, essentially, the standard conditions in which stable nc-AFM imaging may be achieved.

Conversely, the simple model will fail in the following cases:

- interactions between tip, solvent, and surface are not dominated by the interaction with a single water molecule at the apex, e.g., the tip is blunt, the tip comes too close to the surface, or the oscillation amplitude is too large. We note that in any of these situations, stable imaging conditions would also be unlikely.
- the model on which the water density calculations are based fails to reproduce the correct hydration structures on the surface.

Therefore, our model may be useful to AFM experimentalists in two ways:

- using the simple relationship between water density and force on tip, it can be rapidly tested, whether the experimental AFM tip conditions can be approximated by a single water molecule tip (validation of the simple model).
- it can be easily assessed whether the AFM experiment in question is truly capable of resolving individual water molecules in hydration layers, i.e., the interactions between the tip apex and its local environment are dominated by interactions with a single hydration layer water molecule. If not, the images obtained are a convolution of interactions between the tip and multiple water molecules and/or surface atoms.

V. CONCLUSION

In summary, we propose a simple model to describe the tip force from water density. The latter is easily obtained in a calculation, and provides a much faster way to calculate force than by direct computation of force. A practical consequence of this force-water density relation is that, if tips that approximate our suggestion (e.g., sharp covalent or ionic tips that allow hydroxylation or hydration of the tip apex) can be produced reproducibly and used in nc-AFM experiments, then nc-AFM can become a tool to quantitatively probe solvation structure in a non-invasive manner.

VI. METHODS – SUPPORTING INFORMATION

Our simulations were carried out using classical molecular dynamics as implemented in the version 4 series of the GROMACS code.[30] Visualisation and some analysis were carried out using the VMD program.[31] In particular, the *local water density*, $\rho(\mathbf{r})$, used to construct free energy

curves was constructed from counts of water within $0.1 \times 0.1 \times 0.1$ nm^3 cubes, centered at the point $\mathbf{r}$.

The system used for numerical tests of our model was fully solvated fluorite, CaF$_2$, using the setup described in detail in Ref. 16. Importantly for this work, we checked that the quantity of water present is sufficient that the equilibrated water achieves bulk density when far from the surface. This provides a reservoir of water molecules at bulk chemical potential and, equivalently, gives us a well-defined value of the bulk water density, ρ_0.

FEP calculations were carried out using the protocol described in Ref. 16. Briefly, part of the system representing a tip (in this case the O atom of the tip water molecule) is constrained to a fixed point in space. At this point a molecular dynamics simulation is performed and a set of representative configurations saved. The free energy change ΔG to move from point $\mathbf{r}_0$ to point $\mathbf{r}_1$ is then found by perturbing the tip in each of the saved configurations by a rigid translation from point $\mathbf{r}_0$ to $\mathbf{r}_1$ using the relation[24]

$$\Delta G = G(\mathbf{r}_1) - G(\mathbf{r}_0)$$
$$= -k_{\mathrm{B}}T \ln \left\langle \exp\left(-\frac{U(\mathbf{r}_1) - U(\mathbf{r}_0)}{k_{\mathrm{B}}T}\right)\right\rangle_0, \quad (8)$$

where the subscript 0 indicates that the average is taken over the configurations collected when the tip is at point $\mathbf{r}_0$ and the potential energies are calculated at the unperturbed (subscript 0) and perturbed (subscript 1) locations. The total free energy change of the tip approaching the surface is then built up by adding together the individual contributions. Here for a given force curve, say over a cation on the surface, we fix the x and y coordinates of the tip to be the same as the cation, and move the z coordinate of the tip towards the surface in steps of 0.01 nm to cover a range of tip-sample distances of 0–1.2 nm. The force-field describing CaF$_2$ and water-CaF$_2$ interactions was taken from de Leeuw and Cooper,[32] discarding polarization terms. To describe water the TIP4P/2005 model was used.[33] We applied a 0.9 nm cut-off to treat non-bonded interactions and smooth particle mesh Ewald method to treat electrostatics.[34] The equations of motion were integrated using a 2 fs time step, and the LINCS algorithm was used to enforce rigid water geometries. An NPT ensemble (300 K, 1 atm) was generated using Berendsen thermostats and barostats, with time constants of 1.0 and 10.0 ps for temperature and pressure, respectively. The first 0.5 ns of the 4 ns simulations were discarded as equilibration periods.

ACKNOWLEDGMENTS

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