Supplementary Information

Probing Hydrophilic Interface of Solid/Liquid-Water by Nanoultrasonics

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Spatial resolution

In these experiments the spatial resolution is given by the pulsewidth of the acoustic pulse in the interfacial region, and because the acoustic pulse is reflected in the complex interfacial water structure, the resolution is in fact given by half the pulsewidth. With the density and elastic modulus obtained from the fitting of the experimental traces (GaN), we can calculate the effective sound velocity and the effective pulsewidth in the interfacial water region and thus confirm the high resolution in the interfacial region as shown in Fig. S1.

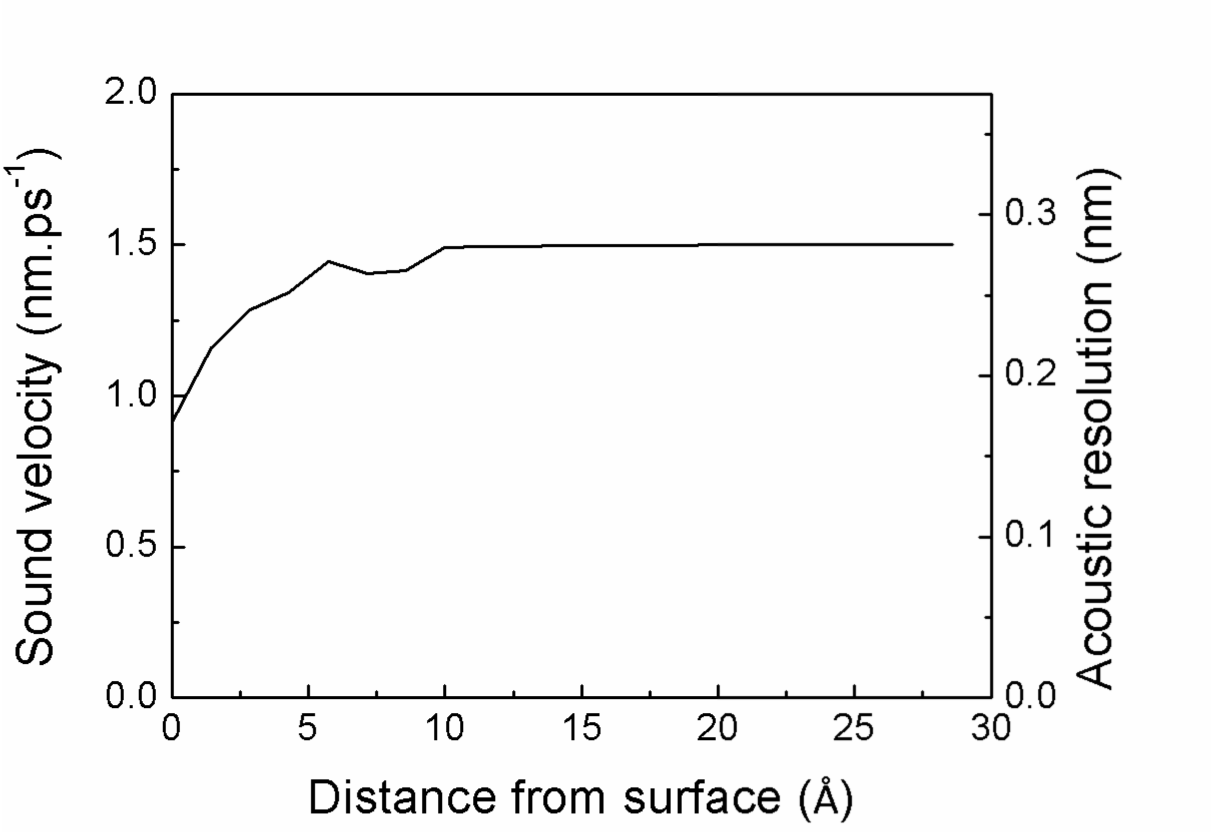

Fig. S1: Acoustic resolution in the interfacial region due to the finite pulsewidth.

However, due to our algorithm, it is possible to obtain an even better spatial resolution. Indeed, in the data analysis, we divide the spectrum obtained for the solid/water interface by the spectrum of the solid/air interface, which is equivalent to performing a deconvolution. Thanks to this deconvolution process, the limit to our resolution is not given by the finite pulsewidth, but by the sampling density and noise in our experimental traces.

Data Fitting

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As shown in Fig. 3a, there are totally 27 free parameters in the model, including the density, ρ, bulk modulus, A, and bulk viscosity, b, of layer j=21 to j=14 and the characteristic length of the exponential decay starting at j=14. These quantities within 1 nm (14<j<21) from solid surface can arbitrarily vary under a converging constrain given by:

If $X_{j-1} > X_{Bulk}$, then $X_J < X_{J-1}$ or $X_j > 1/X_{J-1}$

Or $X_{j-1} < X_{Bulk}$, then $X_J > X_{J-1}$ or $X_j < 1/X_{J-1}$

where X can be ρ, A, or b.

A genetic algorithm (GA) was used to find the best solution and the confidence range of fitting. The initial populations in the GA are the best 1000 sets picked up from a 1 million sets of randomly-valued parameters according to the error defined as the sum of the absolute values of the differences between the experimental and calculated reflectivity and phase. In each generation the 1000 populations will generate another 1000 sets of parameters through mating and mutations and only the best half of the totally 2000 populations can survive at the end of generation. The survived 1000 populations become the initial populations of the next generation. The mating of two populations will generate the arithmetic and geometric averages of the two sets of parameters. The mutation allows the parameter X_j to vary between max (X_{J+1}, $1/X_{J+1}$) and max (X_{J-1}, $1/X_{J-1}$), if $X_J > X_{Bulk}$, or between min(X_{J+1}, $1/X_{J+1}$) and min (X_{J-1}, $1/X_{J-1}$), if $X_J < X_{Bulk}$. The presented results shown in Fig. 3 are the calculation results after 1000 generations.

The error bars that can be seen in Fig. 3 correspond to extrema solutions of the genetic algorithm that give a reflection spectrum within the experimental uncertainties.

Thermal boundary resistance

Scattering of heat carriers at crystal boundary generally causes reduction in the efficiency of energy transport, which is called thermal boundary resistance and is especially important in cryogenics. At low temperature (<1 K), this phenomenon was satisfactorily explained by the acoustic mismatch model based on the continuum acoustic theory with considerations of a prefer interface, while it quantitatively deviated from the expectation at higher temperatures (so-called Kapitza anomaly) [1, 2]. The corresponding anomalous transmission of acoustic phonons at interfaces has been actively studied over the past several decades, and a number of reports suggested that diffuse scattering of high-frequency phonons (>100 GHz) by surface inhomogeneity or irregularity could be a channel resulting in excess transmission [1, 3]. Even with these studies, no generally accepted theory has emerged due to a limited number of detailed experimental works under controlled conditions with a well-characterized surface prepared and studied. Consequently, the dominant mechanism causing the diffuse scattering of high-frequency phonons at a crystal-liquid interface has still been unknown, and the corresponding quantitative description of specular/diffuse scattering probability, the fraction of phonons which are scattered specularly/diffusively, is thus lacked up to date. Exploration of those issues is not only essential for explaining nowadays observations in cryogenics, but also for heat management in nanoscaled objects due to large surface-to-volume ratios.

Transition from normal to anomalous Kapitza resistance typically occurs at 1-10 K, where the dominant phonons for heat transport have frequencies on the sub-THz range (0.09-0.9THz). Observations on the corresponding sub-THz phonon-interface interactions thus provide essential clues to the cause of Kapitza anomaly. In our study, the measured acoustic reflection (or specular scattering) versus phonon frequency can be directly related to the thermal boundary resistance versus effective temperature, which represents the above mentioned anomaly in the resistance to the heat flow at a crystal-liquid interface. Since heat is mostly carried by phonons, the observation of a lower reflection at high frequency reveals a new channel to cause the observed Kapitza anomaly that high frequency phonons more easily transmit heat due to the structuration of water at the interface. According to Ref. [1], the thermal boundary resistance R_b can be approximated by:

$$R_bT^3 = \left(\frac{\pi^2}{15}\frac{k_b^4}{\hbar^3}\sum_j c_{1,j}\Gamma_{1,j}\right)^{-1} \qquad , \quad (1)$$

with

$$\Gamma_{1,j} = \int_0^{\pi/2} \alpha_{1\to 2}(\theta, j)cos(\theta)sin(\theta)d\theta \qquad , \quad (2)$$

where T is the temperature, $c_{1,j}$ is the phonon velocity in medium 1 of the phonon mode *j*, $\alpha_{1\to 2}(\theta, j)$ is the transmission probability of phonon mode *j* with incident angle ϑ. By applying this formula to our case, normal incidence and longitudinal phonon, we can obtain an estimated thermal boundary resistance versus effective temperature that we reproduce in Fig. S2.

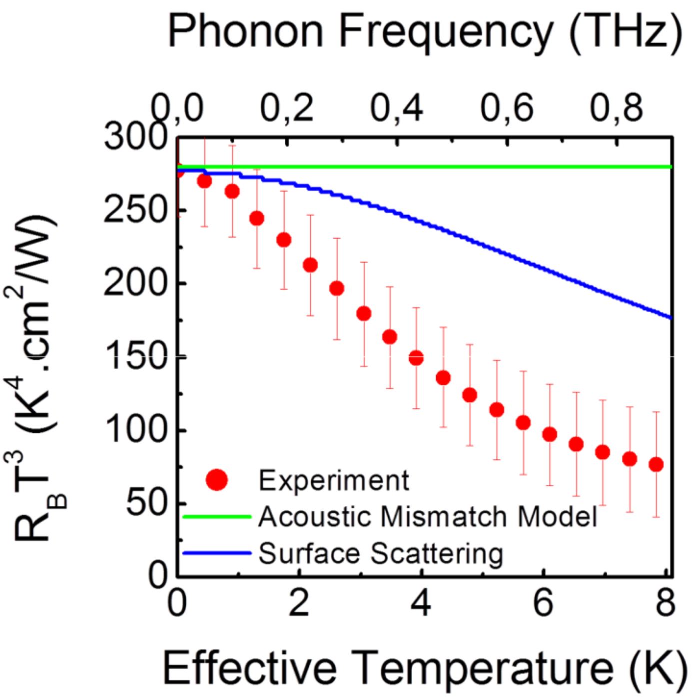

Fig. S2: Estimated thermal boundary resistance (red dots) based on our experimentally measured data assuming that only longitudinal acoustic phonons with normal incidence contribute to the heat transport. Theoretically-calculated thermal boundary resistances obtained using acoustic mismatch model (green line) only and by further considering extra thermal boundary resistance due to the surface roughness (blue line) are also shown for comparison.

We also reproduced the effective thermal boundary resistance expected due to acoustic mismatch model (green line) only and by considering the scattering of phonons by the surface roughness (blue line) [3]. Even though this surface-roughness mechanism also creates a better transmission of heat at higher temperature, it cannot totally explain our observed thermal resistance behavior, confirming the role played by the interfacial liquid structure. After comparing with the result considering the scattering of phonons by the surface roughness, the observation of the further reduced thermal boundary resistance from our experiments at high frequencies (or higher effective temperature) shows the effect of the interfacial water structure that acts like an impedance matching layer, which allows better transmission of 0.2-1THz acoustic phonons into the liquid water. In other words, the interface water structure is partially responsible for the anomalous Kapitza resistance observed in the oxide-water interface in our study.

Nanoultrasonic imaging versus molecular dynamics simulation

Interfacial water has been intensively studied using molecular dynamic simulation. [4, 5] In this study, we use nanoultrasonics to image the interfacial water and different convention is used to describe the system and can lead to discrepancies with the view obtained by molecular dynamics. From the molecular dynamic simulation point of view, the mass density in a perfect crystalline material along a direction is not smooth and can be represented by a succession of delta functions corresponding to atomic planes. However, in acoustics, the mass density in a perfect crystalline material along a direction is a constant and we do not expect to see any acoustic reflection due to the discrete delta functions separated by the distance between atomic planes. These two different ways of studying a similar system leads to different definitions for the parameters of the system, for instance how to define the position of the solid surface. In molecular dynamics, the convention is to consider the surface to be the center of the atomic plane terminating the surface of the solid. This description leads to the appearance of a valley in the density before the first layer of water. For acoustics, this area should not be considered as vacuum and should correspond to the length of the bond between the substrate and the first interfacial water layer. In acoustics, the surface of the solid, as depicted in Fig. S3, is located at the center of the bond between the solid and the liquid. It is well known that acoustic waves do not propagate in vacuum but propagate through bonds. A vacuum area in between the solid and the water would mean that acoustic waves cannot propagate through and will be completely reflected back into the solid. This is against our ultrasonic observation.

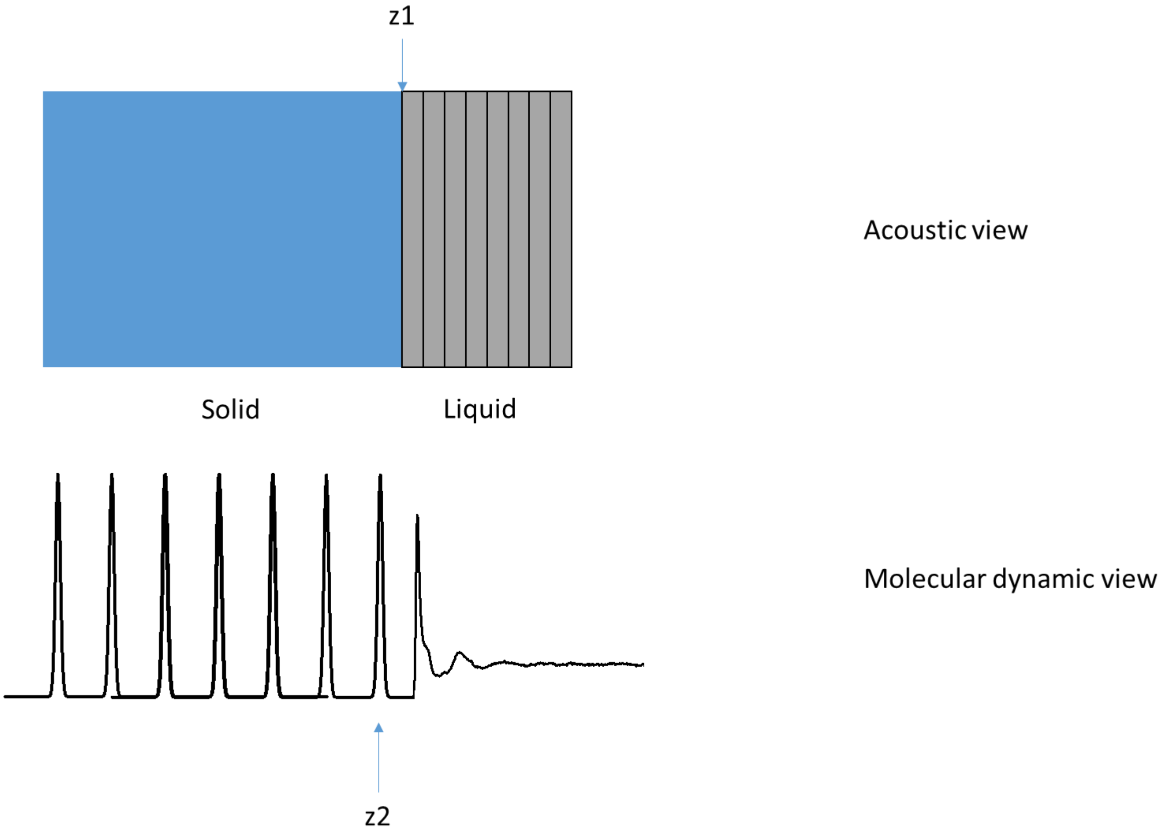

Fig. S3. Comparison between the definition of the position of the surface in the case of a discrete model (Molecular dynamic view) and a continuous model (acoustic view).

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In this manuscript, we have made the choice to shift the position of the surface, so that the distance between the surface and the first water molecules is equal to 2 angstrom, which is approximatively the equilibrium position of water molecules at an oxide surface. [2, 3] By shifting the position of the origin, we have made the comparison with molecular dynamics possible.

Another discrepancy between nanoultrasonics imaging and molecular dynamics concerns the achievable resolution. Indeed, in our study, we use acoustic phonons to probe the structure of interfacial water. The resolution is thus given by the pulsewidth and the wavelength. Thanks to the use of an extremely thin single quantum well, and to the important difference between the sound velocity of GaN and of water, we can reach sub-nanometer resolution (Fig. S1). However, the resolution achieved in this study is never comparable to the spatial resolution of the molecular dynamic simulation, which is infinitely small.

In addition to the limited spatial resolution and the nature of acoustic waves, other factors, specific to our study further influence our observation: surface roughness, which will be discussed in next section, and acoustic attenuation in water. The second factor is highly frequency dependent. Due to the attenuation, our acoustic detection is with a sensitivity function that degrades when getting further away from the interface. We are thus able to resolve accurately the density of the first layer, but we should be less accurate on the profile distribution away from the interface. By achieving the generation of higher frequency acoustic waves and thus higher resolution, and by working with less rough surface, we believe that the technique we developed will be able to observe the expected layering effect of interfacial water on some hydrophilic surfaces.

Influence of surface roughness

In a solid liquid interface, surface roughness is not avoidable and is always playing a role. This roughness leads to the famous Kapitza anomaly. In our experiment, roughness plays an acoustic role (as discussed in the section of thermal boundary resistance), by inducing some scattering of acoustic waves, and also a structural role, by modifying the water organization compared to a sample with an ideally flat surface. By measuring the reflectivity with and without water, we are able to remove the influence of surface scattering from the acoustic point of view and to recover the degradation of our spatial resolution caused by the surface roughness, but not from the structural one. Lots of molecular dynamic simulation on interfacial water predicts a layering effect close to the surface. However, as can be seen in the following figure in which we numbered the water molecules to represent two different layers, with a roughness of 0.5 nm greater than the expected distance between two layers, these two layers starts to be intertwined, and we are thus not able to resolve the second layer due to this surface roughness effect. We can conclude that nanoultrasonic imaging on an atomically flat surface (with a roughness less than the expected distance between two layers) would reveal the fine structure of interfacial water. It is important to mention that, even though roughness plays a role in our result by preventing us to observe the second layer in the density profile, we are able to observe the sub-nanometer features such as the high density or the strong viscosity profiles of the first layer.

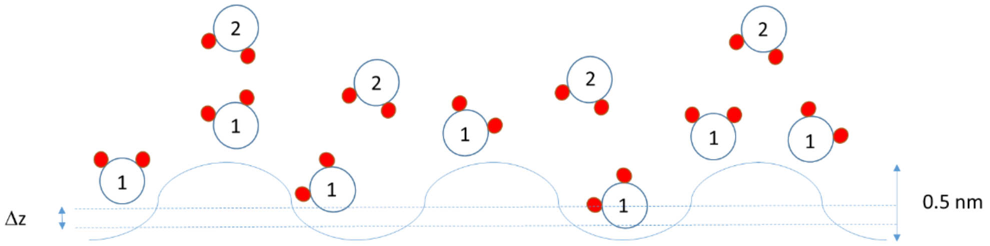

Figure S4. Schematic representation of the structural modifications induced by surface roughness on the interfacial water.

The surface roughness, could also play a role in another discrepancy that can be noticed between our observation and molecular dynamic simulation, which is the average density of the interfacial structure. Indeed, in molecular dynamic simulation, the average density of the interfacial structure is approximately the same as in bulk water. However, in our case, we measure an average density of 1.58 g.cc^{-1} in the first 15 angstrom after the surface. This observation could be contributed by many phenomena. First, as described previously, the decreased sensitivity when moving away from the surface could play a role. Then, the roughness will induce a structural modification of the interfacial structure compared to the case of simulations, in which the surface is often considered atomically flat. Water molecules will be able to bond between layers thus smoothing out the layering effects. Finally, we should also consider the roughness is increasing the surface of interaction between solid and liquid. Therefore it is possible to have more water molecules in a similar area because of the roughness induced increased surface area.

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