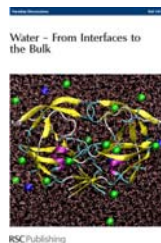


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# Study of a nanoscale water cluster by atomic force microscopy

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We present a novel method for investigating a nanometric cluster of water molecules, which includes the formation and manipulation of nanometric water, and the measurement of its mechanical properties. The atomic force microscope based on the quartz tuning-fork sensor is employed to form and manipulate the nanometric water, and the theoretical tool of amplitude-modulation atomic force microscopy is used to obtain the elasticity, viscosity and dissipation energy of it. With high vertical resolution less than  $\sim 0.1$  nm and high force sensitivity of  $\sim 0.01$  N m<sup>-1</sup>, this tool facilitates the stable formation and manipulation of a nano-water cluster ( $\sim 10^4$  molecules) in air without ‘jump-to-contact’ instability, as well as quantitative measurements of its physico-chemical properties.

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Understanding nanometric water is essential to solve a wide range of common problems in nanoscience and technology such as tribology, scanning probe microscopy (SPM), micro-electro-mechanical systems (MEMS), and biology. Frictions experienced in everyday life are associated with the mechanical properties of nanometric water formed between two surfaces,<sup>1,2</sup> and a water layer of a few nanometers’ thickness existing on every surface affects the performance of SPM and MEMS<sup>3</sup> due to the strong adhesion force.<sup>4</sup> This nanoscale water is also an important environment in biological processes. For example, protein folding and enzyme activation cannot be made without nanometric water both surrounding and confined within the proteins,<sup>5,6</sup> and the ions are transported through a nanometre-sized ion channel which is filled with nanometric water.<sup>7</sup> Due to this ubiquity and importance in nanoscience and nanotechnology, the study on nanoscale water (in general, any liquid) becomes more and more important.

One of the methods to investigate the nanoscale water is ‘touching’ it directly using probe-based techniques such as surface force apparatus (SFA) and atomic force microscopy (AFM). By using SFA,<sup>4</sup> various aspects of nanoconfined liquids were observed; oscillatory solvation force, adhesion force and confinement-induced phase transition of some liquids.<sup>8</sup> However, the detailed behavior of a liquid confined within a tip-sample separation of less than  $\sim 1$  nm could not be measured because of the ‘jump-to-contact’ instability in the region. Moreover, only a 2D liquid film has been considered due to the relatively large probe size ( $\sim 1$   $\mu$ m). Although AFM is capable of investigating a nanoscale-water bridge formed between the tip and sample surface,<sup>9</sup> the conventional cantilever-based AFM also suffers from the ‘jump-to-contact’ instability, so that one can not arbitrarily form and manipulate the nanoscale water in air.

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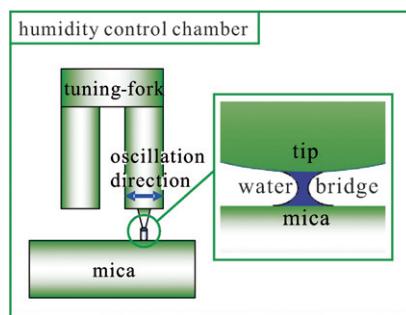
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In this paper, we present a novel method of investigating a nanometric water cluster by using the quartz tuning-fork-based amplitude-modulation (AM) AFM. Combing this technique with related theoretical tools recently developed,<sup>10</sup> we achieve stable formation and manipulation of a nano-cluster of water molecules in air, and perform a quantitative measurement of the elasticity, viscosity and dissipation energy of the nanoscale water.

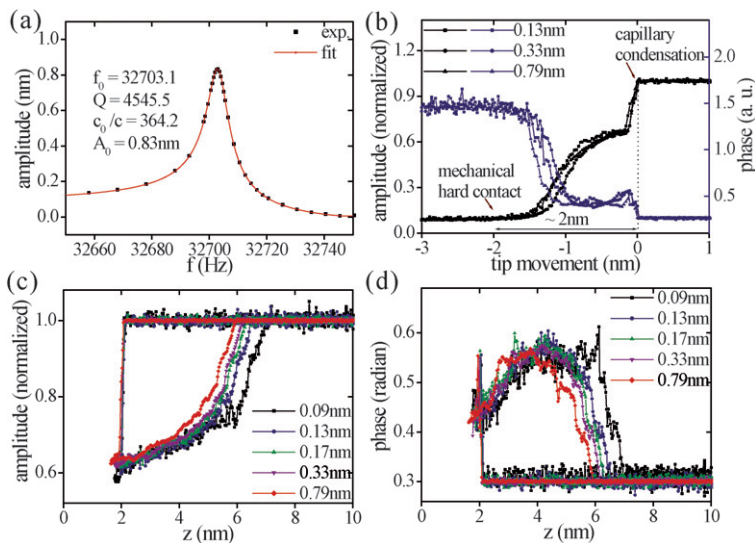
For the study of a nanometric water cluster, it is essential to realize a stable formation of the nanometric water and to perform a sensitive measurement of its properties. This can be achieved by using our novel method; use of the quartz tuning-fork as a force sensor, which exhibits a very strong rigidity of  $\sim 1000 \text{ N m}^{-1}$  as well as a very high quality factor of order  $\sim 1000$ . The high rigidity of the tuning-fork allows stable formation of nanometric water bridge in air by capillary condensation<sup>11</sup> without any 'jump-to-contact' instability. Moreover, it also allows one to perform very sensitive measurements since the high quality factor compensates the decrease of sensitivity due to the rigid spring constant. For a local detection, the tuning-fork actuator is combined with a conventional cantilever tip (100 nm radius,  $n^+$ -silicon, resistivity of 0.01–0.02  $\Omega \text{ cm}$ , Nanosensors), by gluing the cantilever tip on the tuning-fork and then cutting away the leg of the whole body of cantilever except the tip itself. The tuning-fork probe and the mica substrate, prepared by careful chemical cleansing with dilute acid after *in situ* cleavage,<sup>11</sup> are placed in a humidity control chamber, as shown in Fig. 1.

For precise and quantitative measurement, an accurate calibration of the probe properties as well as an unambiguous determination of the absolute zero distance between tip and substrate is required. The probe calibration can be made accurately by fitting the resonance curve to the tuning-fork's resonance function described in ref. 12 (Fig. 2a). On the other hand, the absolute zero point is determined by the full-approach curves (Fig. 2b), where the amplitude and the phase signals exhibit saturation characteristics after about 2 nm movement toward the substrate from the point of capillary condensation, marked as  $z = 0$ . Thereby, we assume the capillary condensation, where the abrupt change of the amplitude and phase signals are observed, occurs at the tip-sample separation of  $\sim 2 \text{ nm}$  in our environmental conditions (relative humidity (RH) = 23%, 18 °C).

Such a calibrated tuning-fork-based AM-AFM is now used for a stable formation of a nano-cluster of water molecules in the following way. The laterally oscillating AFM tip approaches the substrate within a few nanometre distance until capillary condensation occurs, which produces a few-nanometre-sized bridge of water molecules between the tip and the substrate. Once the capillary condensation has occurred, it is stretched vertically upward by subsequent retraction of the tip to avoid the mechanical hard contact with the substrate. During these procedures, the amplitude and the phase changes are recorded, from which true mechanical



**Fig. 1** Schematic diagram of tuning-fork-based atomic force microscope in a humidity chamber.

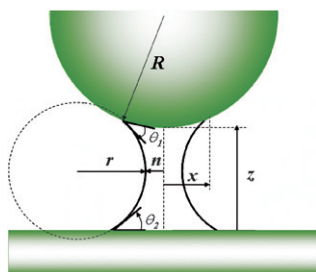


**Fig. 2** (a) Free resonance curve of the tuning-fork probe and its fit to the model described in ref. 12. (b) Full approach curves for different free oscillation amplitudes;  $A_f = 0.13, 0.33$  and  $0.79$  nm. (c) and (d) The amplitude and the phase changes during the tip approach and subsequent retraction ( $v \approx 1$  nm  $s^{-1}$ ) for various free oscillation amplitudes  $A_f = 0.09, 0.13, 0.17, 0.33$  and  $0.79$  nm on a fixed operating frequency,  $f = 32\,702$  Hz.

signals are obtained by using the formulae described in ref. 12 to remove the artifact signals which occur in quartz resonators.

Fig. 2c and 2d show the mechanical motion of the probe, the amplitude and the phase, where we set the capillary condensation point to  $z = 2$  nm, as noted above (Fig. 2b). The probe is operated at the frequency  $f = 32\,702$  Hz and approaches or retracts with velocity of  $v \approx 1$  nm  $s^{-1}$ , which is far faster than the thermal drift of the system  $v_{\text{drift}} \approx 0.03$  nm  $s^{-1}$ . When the capillary condensation has occurred, the amplitude and the phase signals are abruptly changed and then gradually recovered as the tip is retracted to the rupture points, exhibiting hysteresis. These are the characteristic features of the capillary interaction because any other force between the tip and the substrate, such as the van der Waals (vdW) or electrostatic interactions, are exerted on the probe rather gradually, not abruptly, and also do not exhibit the hysteresis.<sup>13</sup> Interestingly, the rupture distance is increased little by little with the decrease of free oscillation amplitude  $A_f$ , which indicates that a more stable formation of the nanometric water bridge is made when a smaller oscillation amplitude is used.

The nanometric water bridge formed between the tip and the substrate can be modeled by sphere-flat geometry,<sup>14</sup> as shown in Fig. 3, where  $R$  is the tip radius,  $x$



**Fig. 3** Schematic of a sphere on a flat surface with a liquid meniscus between them.

the contact point between the tip and the liquid,  $z$  the tip–sample distance, and  $n$  and  $r$  the two principal radii. The contact angles,  $\theta_1$  and  $\theta_2$ , are usually assumed to be zero;  $\theta_1 = \theta_2 = 0$ , for the hydrophilic Si tip and for the mica sample. For a given  $z$ , two parameters,  $n$  and  $r$ , can be uniquely determined once the meniscus volume is determined, which can be done by using the relation Willett *et al.*<sup>15</sup> have found on the basis of numerical solutions of the Young–Laplace equations,

$$z_r = (1 + \theta/4)V^{1/3} - \frac{2}{5R}(1 + \theta/4)V^{2/3}, \quad (1)$$

where  $z_r$  is the rupture distance,  $V$  the volume of water bridge,  $R$  the tip radius, and  $\theta$  the contact angle in radians ( $\theta = \theta_1 = \theta_2$ ). For our rupture distance of  $\sim 6.5$  nm (Fig. 2c and 2d), a liquid volume of  $297.9$  nm<sup>3</sup> is obtained (about 36 000 molecules of water).

We note that the rupture distance of 6.5 nm is not satisfied with the Kelvin equation,<sup>16,17</sup> which requires a Kelvin radius of curvature  $r_k = -0.37$  nm to remain constant value under the given temperature and relative humidity in our experiment, and from which a rupture distance of  $z_r = 0.32$  nm is predicted for the zero contact angles. Thus, the nanometric water bridge formed in our experiments does not satisfy the boundary condition of constant curvature expected by the Kelvin equation, which indicates that the liquid phase does not remain in equilibrium with the vapor, but liquid–vapor exchanges are negligible during the subsequent retraction of the tip after the capillary condensation is occurred. For the latter case, the constant volume boundary condition is available, which is now employed to analyze the thermodynamics of our nanometric water bridge with the following equations:<sup>16,17</sup>

$$(R + r)^2 = (n + r)^2 + (R + z - r)^2, \quad (2)$$

$$p = \gamma \left( \frac{1}{n} - \frac{1}{r} \right), \quad (3)$$

$$F_c = p(n + r)^2\pi, \quad (4)$$

$$F_t = 2\pi\gamma \frac{R(n + r)}{R + r}, \quad (5)$$

where eqn (2) is the constraint of our system given by the zero contact angle,  $p$  the Laplace pressure,  $F_c$  the capillary force induced by the Laplace pressure,  $\gamma$  ( $= 72.8$  mJ m<sup>-2</sup>) the surface tension for water at 20 °C, and  $F_t$  the surface tension force induced by surface tension.

The thermodynamic parameters calculated from eqn (2), (3), (4) and (5) are shown in Table 1, where the nominal values for the capillary condensation and the rupture distances were chosen as 2.00 nm and 6.50 nm, respectively.<sup>18</sup> The negative sign of  $p$  represents the concave shape of the bridge as well as the attractive force between two surfaces. While the Laplace pressure  $p$ , or equivalently  $F_c$ , has the negative value at the capillary condensation point, it is changed to be a positive one at the rupture distance. This means that when the nano-bridge is formed, it exerts high attractive force (approx.  $-8.9$  nN) between the two surfaces, and then it becomes thin and long reducing the attractive force during its stretch. But near  $z \approx 6.5$  nm the attractive force is changed to the repulsive one ( $\sim 0.3$  nN), whereby the nano-bridge becomes highly unstable so that it is ruptured.

Interestingly, even at the rupture point, the neck radius  $n$  has a small but finite value of  $\sim 3$  nm. Although this critical value of rupture width is obtained by classical

**Table 1** Thermodynamic parameters of the nanometric bridge of  $\sim 36\,400$  water molecules formed between the tip and the substrate. The condensation and rupture distances  $z$  are set at 2 nm and 6.50 nm respectively, from which  $r$ ,  $n$ ,  $p$ ,  $F_c$  and  $F_t$  are calculated by using eqn (2), (3), (4) and (5) with the boundary conditions of constant volume and zero contact angle

	Condensation	Rupture
$z/\text{nm}$	2.00	6.50
$r/\text{nm}$	1.13	3.35
$n/\text{nm}$	6.22	2.98
$x/\text{nm}$	7.27	6.12
$p/\text{MPa}$	-52.5	2.7
$F_c/\text{nN}$	-8.9	0.3
$F_t/\text{nN}^a$	3.3	2.8
$F_c/F_t$	-2.7	0.1

<sup>a</sup> Surface tension force  $F_t$  is exerted on the tip surface in the radial direction, which results in a vertical attractive force.

thermodynamic theory, it is also in agreement with the theoretical results based on the lattice gas Monte Carlo simulations.<sup>20</sup> We also note that about 1 nm slip ( $x = 7.27 \rightarrow 6.12$  nm) of contact line between the tip surface and the liquid phase is occurred during the stretch up to rupture distance, which is often revealed by the ‘stick-slip’ behavior of mechanical friction.<sup>11</sup>

Mechanical properties of the small cluster of water molecules can be obtained with the theory of AM-AFM,<sup>10</sup> by substituting the amplitude and the phase information in Fig. 2c and 2d into the following set of equations for the elasticity  $k_{\text{int}}$ , viscosity  $b_{\text{int}}$ , elastic force  $F_k$ , viscous force  $F_b$  and dissipation energy  $E_{\text{dis}}$ :

$$\frac{k_{\text{int}}}{k} = \frac{A_0}{QA} \sin\theta + \left(\frac{w}{w_0}\right)^2 - 1, \quad (6)$$

$$\frac{b_{\text{int}}}{b} = \frac{w_0 A_0}{wA} \cos\theta - 1, \quad (7)$$

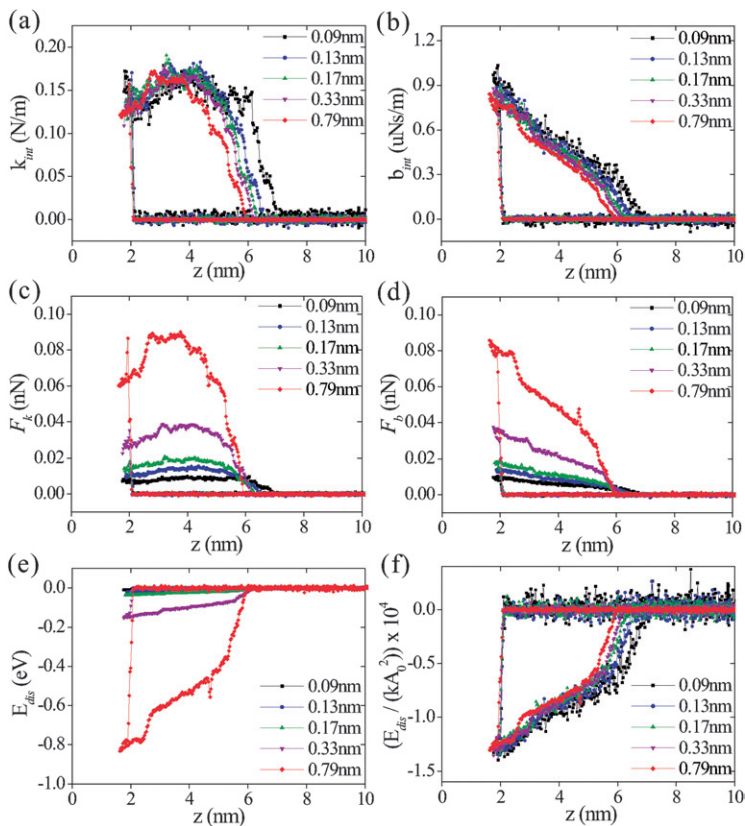
$$F_k = k_{\text{int}}A, \quad (8)$$

$$F_b = b_{\text{int}}wA, \quad (9)$$

$$\frac{E_{\text{dis}}}{kA_0^2} = -\frac{\pi}{Q} \left[ \frac{A}{A_0} \cos\theta - \frac{w}{w_0} \left( \frac{A}{A_0} \right)^2 \right], \quad (10)$$

where  $A$  and  $\theta$  are the amplitude and the phase of tip motion respectively,  $A_0$  is the peak amplitude at the resonance frequency  $w_0$ ,  $w$  the operating frequency, and  $Q$  the quality factor of the probe. The rigidity of the probe  $k$  ( $= 1478.2 \text{ N m}^{-1}$ ) can be obtained either by theoretical calculation<sup>19</sup> or thermal spectrum, and the damping coefficient  $b$  of the free space is given by  $b = kl/(Qw_0)$ . We note that eqn (6) and (7) are corresponded to the first-order solution of the tapping-mode configuration of AM-AFM,<sup>10</sup> which are still available and generally work in this shear-mode configuration as shown in ref. 12.

Fig. 4 presents  $k_{\text{int}}$ ,  $b_{\text{int}}$ ,  $F_k$ ,  $F_b$  and  $E_{\text{dis}}$  of the nanometric water column. It is clearly shown that the measured  $k_{\text{int}} \approx 0.1 \text{ N m}^{-1}$  and  $b_{\text{int}} \approx 0.6 \text{ }\mu\text{N s m}^{-1}$  are



**Fig. 4** Mechanical properties of nanometric cluster of water molecules: elasticity (a), viscosity (b), elastic force (c), viscous force (d), dissipation energy (e), and dissipation energy normalized by  $kA_0^2$  (f) obtained from the amplitude and the phase curves in Fig. 2c and 2d.

not much dependent on the measured amplitudes in the range from 0.1 nm to 1 nm, which manifests the linear characteristics of  $F_k$  and  $F_b$  that are linearly increased with increasing the oscillation amplitude. Although frictions which are experienced by an object sliding on a surface have been macroscopically believed to be proportional to the velocity of the object motion, the probe shearing the mica surface experiences the velocity-dependent force  $F_b$  (Fig. 4d) as well as displacement-dependent force  $F_k$  (Fig. 4c). Moreover, almost same amount of forces are contributed by  $F_k$  and  $F_b$  to the friction. This is due to the viscoelasticity,  $k_{\text{int}}$  and  $b_{\text{int}}$ , of the nanometric water cluster between two surfaces.

The measured damping  $b_{\text{int}} \approx 0.6 \mu\text{N s m}^{-1}$  at  $z = 3 \text{ nm}$  is 10 times greater than the hydrodynamic damping acting on the tip moving on a bulk fluid with the bulk constant viscosity ( $\eta_{\text{water}} \approx 10^{-3} \text{ Pa s}$ ), which leads to a damping of  $b_{\text{water}} \approx 0.06 \mu\text{N s m}^{-1}$  at  $z = 3 \text{ nm}$ .<sup>21,22</sup> The  $b_{\text{int}}$ , or  $F_b$ , causes a dissipation energy  $E_{\text{dis}}$  of order 0.1 to 1 eV, of which the origin is different from the one of the dissipation of order  $\sim 10 \text{ eV}$  induced by the condensation–rupture process during each oscillation cycle in large amplitude operation, suggested in ref. 23. On the other hand,  $b_{\text{int}}$  as well as  $k_{\text{int}}$  of the nanometric cluster of water observed in our experiment seem to be intrinsic quantities associated with boundary surface tension and internal structure of the hydrogen bonding network.

In conclusion, the presented method utilizing quartz tuning-fork-based AM-AFM and the developed theoretical tools available allow stable formation and



manipulation of the nanometric water cluster as well as quantitative measurement of its thermodynamic–mechanical properties. Due to the reliable small amplitude operation of our experimental system, this technique enables one to perform a non-perturbative measurement, providing very intrinsic properties ( $k_{\text{int}}$  and  $b_{\text{int}}$ ) associated with the hydrogen bonding network of a nanoscale water cluster rather than the tip-motion-induced ones, such as the large tip-motion-induced dissipation energy.<sup>23</sup> These novel measurements may provide a useful means of extending our understanding of hydrogen bonds in the nanoscale and their cooperative effects in a small water nanocluster,<sup>24</sup> with which numerous anomalies including the large heat capacity, high thermal conductivity and high melting, boiling and critical points are closely associated.

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## References

- 1 J. Chen, I. Ratera, J. Y. Park and M. Salmeron, *Phys. Rev. Lett.*, 2006, **96**, 236102.
- 2 K. B. Jinesh and J. W. M. Frenken, *Phys. Rev. Lett.*, 2006, **96**, 166103.
- 3 C. H. Mastrangelo, *Tribol. Lett.*, 1997, **3**, 223.
- 4 J. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 2003.
- 5 M. S. Cheung, A. E. Garcia and J. N. Onuchic, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 685.
- 6 G. A. Papoian, J. Ulander, M. P. Eastwood, Z. Luthey-Schulten and P. G. Wolynes, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 3352.
- 7 Y. J. Jeon, H. Kim, S. Jon, N. Selvapalam, D. H. Oh, I. Seo, C. S. Park, S. R. Jung, D. S. Koh and K. Kim, *J. Am. Chem. Soc.*, 2004, **126**, 15944.
- 8 J. Klein and E. Kumacheva, *Science*, 1995, **269**, 816.
- 9 R. Szoszkiewicz and E. Riedo, *Phys. Rev. Lett.*, 2005, **95**, 135502.
- 10 Mahee Lee and Wonho Jhe, *Phys. Rev. Lett.*, 2006, **97**, 036104.
- 11 H. Choe, M.-H. Hong, Y. Seo, K. Lee, G. Kim, Y. Cho, J. Ihm and W. Jhe, *Phys. Rev. Lett.*, 2005, **95**, 187801.
- 12 M. Lee, J. Jahng, K. Kim and W. Jhe, *Appl. Phys. Lett.*, 2007, **91**, 023117.
- 13 N. Hashemi, H. Dankowicz and M. R. Paul, *J. Appl. Phys.*, 2008, **103**, 093512.
- 14 T. Stifter, O. Marti and B. Bhushan, *Phys. Rev. B*, 2000, **62**, 13667.
- 15 C. D. Willett, M. J. Adams, S. A. Johnson and J. P. K. Seville, *Langmuir*, 2000, **16**, 9396.
- 16 O. H. Pakarinen, A. S. Foster, M. Paaanen, T. Kalinainen, J. Katainen, I. Makkonen, J. Lahtinen and R. M. Nieminen, *Model. Simul. Mater. Sci. Eng.*, 2005, **13**, 1175.
- 17 A. Chau, S. Rignier, A. Delchambre and P. Lambert, *Model. Simul. Mater. Sci. Eng.*, 2007, **15**, 305.
- 18 Although the tip–sample distances for the capillary condensation and the rupture are estimated roughly, it is found that a small variation of the values does not affect the results presented here including finite rupture width, positive Laplace pressure at the rupture point, and slip behavior on the tip surface.
- 19 F. J. Giessibl, *Appl. Phys. Lett.*, 1998, **73**, 3956.
- 20 J. Jang, G. C. Schatz and M. A. Ratner, *Phys. Rev. Lett.*, 2004, **92**, 085504.
- 21 Olga I. Vinogradova, *Langmuir*, 1995, **11**, 2213.
- 22 Here we used the approximated solution for hydrodynamic damping,  $b = 6\pi\eta R^2/z$ , where  $b$  is the damping coefficient,  $\eta$  the bulk viscosity,  $R$  the tip radius, and  $z$  the tip–sample distance, as described in ref. 21.
- 23 E. Sahagun, P. Garcia-Mochales, G. M. Sacha and J. J. Saenz, *Phys. Rev. Lett.*, 2007, **98**, 176106.
- 24 F. N. Keutsch and R. J. Saykally, *Proc. Natl. Acad. Sci. U. S. A.*, 2001, **98**, 10533.