

Nanoscale patterning of ionic self-assembled multilayers

Aysen Tulpar¹, Zhiyong Wang^{2,5}, Chang-Hyun Jang¹,
Vaibhav Jain³, James R Heflin⁴ and William A Ducker^{1,6}

¹ Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA

² Department of Electrical and Computer Engineering, Virginia Tech,
Blacksburg, VA 24061, USA

³ Macromolecular Science and Engineering, Virginia Tech, Blacksburg, VA 24061, USA

⁴ Department of Physics, Virginia Tech, Blacksburg, VA 24061, USA

E-mail: wducker@unimelb.edu.au

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Abstract

Films that are nanostructured in all three dimensions can be fabricated by the templated growth of ionic self-assembled multilayers (ISAMs) on solids that have been patterned by nanografting. Nanografting was used to controllably pattern –COOH surface groups on a background of –OH groups. Atomic force microscopy (AFM) confirms that ISAM bilayers grow selectively on the –COOH groups and not on the surrounding –OH groups. The patterned area clearly shows an increase in height with an increase in the number of bilayers. As compared with other methods of nanofabrication, nanografting with ISAM deposition provides fast and precise control over the size of the pattern region, which remains stable even after repeated washing. This combination allows the fabricated template to be altered *in situ* without the need of any kind of mask, expensive probe, or post-lithography processing/cleaning methods. We have demonstrated line widths of 75 nm. Ultimately the line width is limited by the width of the AFM tip that causes desorption of the thiol, which is typically about 25 nm. Smaller line widths should be possible with the use of sharper AFM tips.

(Some figures in this article are in colour only in the electronic version)

The fabrication of ISAMs through layer-by-layer (LbL) deposition is a powerful, simple, and rapid approach for the nanoscale control of thickness and composition of thin films in the vertical dimension. ISAMs are formed by the alternating deposition of opposite, multiple-charged species from aqueous solutions onto a substrate [1, 2]. These films have been utilized in a vast array of applications including nonlinear optics [3], photovoltaics [4], electrochromics [5], and antireflection coatings [6]. Because the ISAM deposition technique does not introduce patterning in the dimensions parallel to the substrate, it is typically restricted to applications where films are only required to have structure normal to the interface. However, there is no intrinsic reason why the LbL

method cannot be performed on a patterned substrate so that a complex three-dimensional structure can be developed, in which the lateral dimensions are determined by the patterning of the solid and the vertical structure is determined by the LbL method. It is only necessary to have selective adsorption of the ISAM polymers on one part of the pattern, and this can be achieved by the patterning of charged groups on the solid. Indeed, there have been three previous studies of ISAM formation on patterned substrates. Hammond and colleagues have demonstrated an approach in which the solid is altered by micro-contact printing [7, 8], while Lvov and colleagues have utilized photolithography to pattern the films [9, 10]. In both of these methods, the feature sizes are in the range of hundreds of nanometers to microns. The remaining task is to shrink the size of the lateral patterning so that smaller scale features can be produced. Recently, Mirkin and colleagues have fabricated patterned ISAM surfaces with 80 nm resolution by prepatterning the solid with thiols

⁵ Present Address: GE Global Research Center, Schenectady, NY 12309, USA.

⁶ Author to whom any correspondence should be addressed. Present address: Department of Chemical and Biomolecular Engineering, University of Melbourne, Victoria 3010, Australia.

using dip pen nanolithography (DPN) [11, 12]. Ivanisevic and colleagues used polyelectrolytes as a DPN ink on a silica substrate to develop the template by ISAM assembly fabrication [13, 14].

One limitation of dip pen lithography is that only a single chemical can be written onto the solid with each cantilever, and another is that the width of pattern is limited by the width of the capillary that is formed around the AFM tip. In this work, we employ the nanografting technique [15–17] of AFM to pattern the solid before forming the ISAM film. In nanografting, an AFM tip is used to remove part of an organic monolayer that sits under an AFM tip, and the vacant sites are then backfilled with a different organic monolayer. The resolution of the lines drawn with this technique is related to the width of the tip, and is typically about 25 nm. Nanografting can produce smaller linewidths compared to DPN because the line width depends on the width of the AFM tip rather than the width of the capillary that surrounds the tip. In addition, the nanografting procedure can be used to ‘write’ a variety of different molecules with a single AFM tip, simply by changing the solution in which the writing is performed, i.e. it does not require nanoscale or even microscale plumbing or other intervention to allow the writing of nanoscale features. Thus the combination of nanografting and ISAM deposition can in principle offer very fine scale (<25 nm lateral, <1 nm vertical) control of patterning at interfaces. Such three-dimensional structures with nanoscale features in each dimension could have applications in nanoelectronics, where carbon nanotubes, inorganic nanorods, or regions of semiconducting polymer can be precisely deposited between electrodes, or nanofluidics, where the regions between the ISAM structures can serve as the fluidic channels. The aim of this paper is to demonstrate a patterning method that is a route to these applications.

The procedure is shown schematically in figure 1. The templating patterns are created on clean gold substrates through the adsorption of thiols. The pattern in the thiol film is prepared by first adsorbing an alkanethiol with an ω -OH group. This initial layer is the ‘background’ on which subsequent patterning is performed using pressure applied by an AFM tip. Pressure is applied by the tip to selective areas in a solution of thiol molecules containing a ω -COOH group. The applied pressure causes the desorption of the ω -OH thiol, which is then replaced by adsorption of ω -COOH thiol. In this way, we can produce a pattern of ω -COOH groups on an ω -OH background. This combination of ω -groups was chosen to encourage selective adsorption of a cationic polyelectrolyte on the patterned surface but not on the background. A wide variety of ω -groups has been utilized in the preparation of gold-thiol monolayers, so this technique should be quite versatile for adsorption of different ISAMs.

Figure 2 shows the successful production of the patterned ionic assemblies. The AFM image on the left is taken in water after the nanografting, but before the ISAM deposition process. The yellow (bright) are regions of 16-mercaptohexadecanoic acid (ω -COOH) and the brown regions are 1-mercapto-undecanol (ω -OH). The height difference between the ω -OH and ω -COOH is <1 nm and is caused by a difference in force as well as a real difference in height,

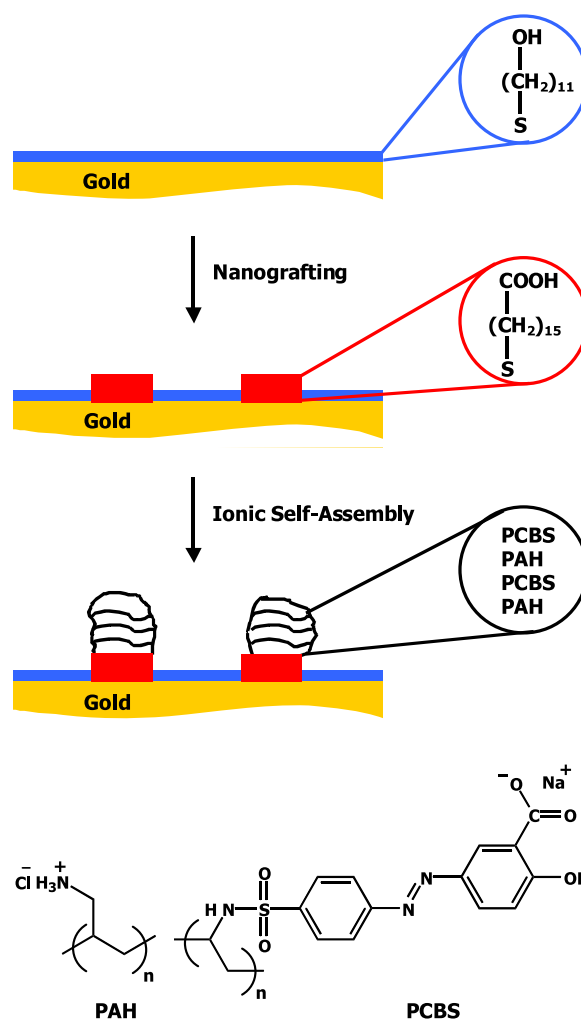


Figure 1. Schematic of the procedure for preparation of polyelectrolyte multilayer films with nanometer-scale patterning in the dimension parallel to the interface.

arising from the difference in the alkyl chain length of the thiol molecules. The surface is then sequentially exposed to aqueous solutions of poly(allylamine hydrochloride) (PAH) and poly[1-[4-(3-carboxy-4-hydroxyphenylazo)-benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PCBS) in the AFM fluid cell. The AFM image on the right is taken in water after the growth of two bilayers of polyelectrolyte (PAH–PCBS–PAH–PCBS) in the fluid cell of the AFM. The increase in height upon deposition of the polyelectrolyte multilayers on the patterns is 3 ± 2 nm. For four ISAM bilayers, the height difference is 7 ± 2 nm. Thus, the added height of the polyelectrolyte approximately doubles when we double the number of layers. In principle many layers could be added by this method. Because the patterning relies on selective adsorption, we expect that ultimately there will be some accumulation of polymers on the surrounding areas.

The film structure is also sensitive to AFM imaging in contact mode. After the deposition of the polyelectrolyte multilayers, the cell was rinsed several times with water, and the surface was imaged in contact mode at a very low force to find the patterns on the surface. Imaging in contact mode at

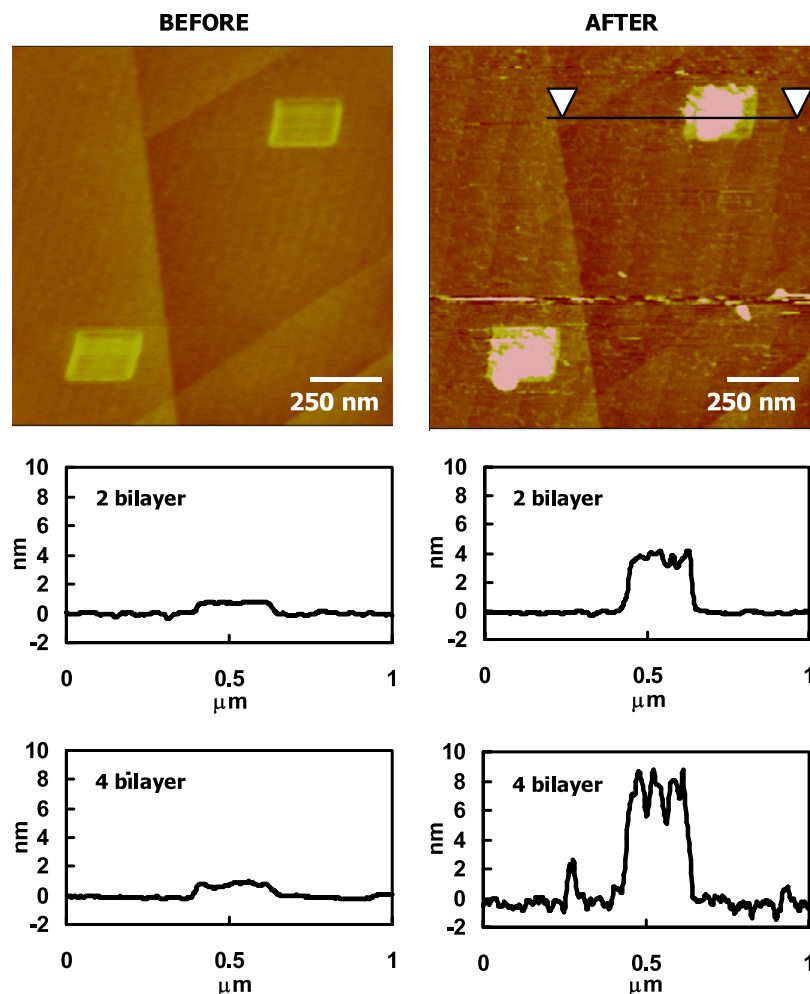


Figure 2. Tapping mode AFM height images of patterned surfaces in water, and the corresponding cross-sectional height profiles. The upper set of profiles corresponds to the images, and the lower set shows the profile when two and four bilayers are deposited.

a low force has the benefit of removing any nonspecifically adsorbed polymers on the background SAM. However, it is difficult to obtain high quality images of the polyelectrolyte multilayers formed on the nanografted patterns with contact mode imaging because, over time, thermal drift leads to changes in the imaging force. An increase in imaging force can also damage the film. It is easier to switch to tapping mode AFM with the same tip immediately after finding the nanografted patterns on the surface.

We investigated the effect of changing the spacer unit in the thiol monolayer. Figure 3 shows a patterned ISAM film that was built on a thiol pattern, created from thiols containing ethylene oxide groups ($\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_6\text{OCH}_2\text{CO}_2\text{H}$ pattern on $\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_3\text{OH}$ background). These thiols can clearly also be used for templating the surface pattern. To compare the deposition effects of polyelectrolytes, the film shown in figure 3 was obtained by a slightly different procedure. The LbL assembly was performed outside the AFM cell (i.e. after the nanografting, the gold sample was removed from the AFM fluid cell, the ISAM assembly was done in a beaker, and then the gold sample was reinserted into the AFM for analysis). This procedure is somewhat tedious because it takes time to find the patterned section of

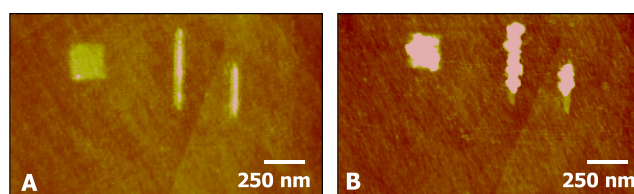


Figure 3. Tapping mode AFM height images of patterned surfaces in water. (A) Nanografted pattern of $-\text{COOH}$ in $-\text{OH}$. The $-\text{COOH}$ pattern is about 0.7 nm 'higher' than the $-\text{OH}$ background. (B) ISAM grown on the pattern produced in (A). The height difference between the $-\text{OH}$ SAM and the polyelectrolyte multilayers on the patterns is 6 ± 2 nm.

the gold substrate, but this is only for verification and is not part of the fabrication process. However, a more thorough rinsing of the gold substrate is possible outside the AFM cell, and using this procedure we did not need to lightly image the surface to remove stray polyelectrolyte that adsorbed on the $-\text{OH}$ background. That is, selectivity in adsorption was assisted by either light imaging or thorough rinsing. The weak deposition on the $-\text{OH}$ background is not robust, and could potentially be prevented entirely through a better choice of

functional groups. It is anticipated that the amount of weakly bound, nonspecifically-adsorbed polyelectrolyte can be greatly reduced by judicious choice of polyelectrolytes, background SAM, and the rinsing and deposition solvents.

Examination of figures 2 and 3 also show that (a) it is possible to produce different shapes on the surfaces (e.g., lines and squares); (b) the templating in this initial demonstration is not perfect: there are regions where the polyelectrolyte spills over the template, and also regions where the polyelectrolyte does not cover the template; and (c) the thicknesses of the polyelectrolyte multilayers when confined laterally on the nanometer-scale are 1–1.5 times greater than when they form a large-area sheet on a surface. (Ellipsometry measurements show that the thickness per bilayer of PAH and PCBS at pH 7 for a large-area film is ~ 1.2 nm [18].) The bilayer thickness of ISAM films is strongly dependent on the pH and ionic strength of the deposition solutions as a result of electrostatic screening and charge neutralization of the polyelectrolyte ions [11, 19]. Confinement of both the thiol template and the polymer to nanometer-scale patches may also alter the polymer conformation and thickness. Studies are ongoing to determine the effect of pH, ionic strength, polyelectrolyte molecular weight, and polyelectrolyte structure on the ability to adsorb multilayers more conformally onto the patterned template. The technique can in the future be used in combination with computer-assisted design (CAD) [20] and massively parallel AFM tips [21, 22] (as high as 55 000 cantilevers) to pattern large (cm) areas with the high (20 nm) resolution demonstrated here.

In summary, we show that the combination of nanografting, to produce patterning in the dimensions parallel to a solid surface, and ionic self-assembly, to produce patterning in the dimension normal to the surface, can be used to produce complex three-dimensional structures in films with nanoscale control in all three dimensions. The linewidth is ultimately limited by the width of the AFM tip, but will also depend on the details of the polymers and solution conditions. For example, a high ionic strength should lead to the formation of less compact polymer films. The large variety of chemical functionalities that can be incorporated using each of these techniques, and the ease with which nanografting can produce features with different shapes, should enable the technique to produce films with a variety of different structures. As with other serial nanolithography approaches, such as electron-beam lithography and scanning tunneling lithography [23], the main drawback of the technique is the time required to draw the patterns on the surface. However, the development of cantilever array techniques will greatly enhance the speed of AFM lithography. In addition, our technique should prove to be valuable, enabling research tool for fabrication and characterization of nanoscale devices in electronics, sensors and other areas.

1. Experimental details

1.1. Materials

1-mercapto-undecanol (Sigma-Aldrich, St Louis, MO) and 16-mercapto-hexadecanoic acid (Sigma-Aldrich, St Louis,

MO) were used as received. NaOH (Aldrich, Milwaukee, WI) was roasted in air at 400 °C for 16 h. HCl (Fischer Scientific, Fairlawn, NJ) was used as received. Poly(allylamine hydrochloride) (Sigma-Aldrich, St. Louis, MO) and poly[1-[4-(3-carboxyl-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediy], sodium salt] (Sigma-Aldrich, St Louis, MO) were used as received. HS(CH₂)₁₁(OCH₂CH₂)₃OH and HS(CH₂)₁₁(OCH₂CH₂)₆OCH₂CO₂H were gifts from Professor Michael Calter (Department of Chemistry, Wesleyan University, Middletown, CT) and were used as received. The gold wires were purchased from Alfa Aesar, Ward Hill, MA. The gold samples for AFM measurements were fabricated as described previously [24].

1.2. Solutions

1-mercapto-undecanol, HS (CH₂)₁₁(OCH₂CH₂)₃OH and HS(CH₂)₁₁(OCH₂CH₂)₆OCH₂CO₂H solutions (2 mM) were prepared with 200 proof ethanol. 16-mercapto-undecanoic acid solutions (0.1 mM) were prepared with 10% acetic acid/ethanol to reduce the physisorbed thiol molecules on SAM surfaces. Polyelectrolyte solutions (10 mM with respect to the monomer unit) were prepared with nanopure water (EASYpure UV, Barnstead Thermolyne Corp., Dubuque, IA). NaOH and HCl were used to adjust the pH of the solutions to pH ~ 7 . Hydrogen ion activities were determined by a pH meter (Orion, Beverly, MA). Measurements were made relative to standard buffers of potassium hydrogen phthalate, pH 4.01 (Orion, Beverly, MA), pH 7.01 (Orion, Beverly, MA), and pH 10.01 (Orion, Beverly, MA).

1.3. Layer-by-layer (LbL) assembly

The first layer is designed to selectively attach to the patterned features on the surface. Thus, we use PAH as the first layer because the electrostatic attraction to –COOH provides selectivity in adsorption on this patterned surface compared to the neutral –OH background. First, PAH solution is injected into the fluid cell of the AFM and is left to adsorb for 3 min., then the cell is rinsed with water ten times. Secondly, PCBS solution is injected, and is left to adsorb for 3 min, then the fluid cell is rinsed with water ten times. This procedure is repeated until the desired number of layers is formed on the surface.

1.4. Atomic force microscopy (AFM)

Nanografting and imaging were performed with an AFM (Veeco Metrology, Santa Barbara, CA). Ultrasharp silicon nitride cantilevers (Park Scientific Instruments) with a force constant of 0.5 N m⁻¹ and a radius of <20 nm were used for both imaging and patterning. The scan parameters were scan lines of 512 (constant) with a scan rate of 1 Hz for both scanning (2.01 $\mu\text{m s}^{-1}$ for 1 μm scan area) and patterning (tip velocity varies with the size of the pattern). Before each experiment, the cantilevers were irradiated for 30 min in a laminar flow cabinet with ultraviolet light (~ 9 mW cm⁻² at 253.7 nm) generated from a PENRAY Lamp (UVP, Inc., Upland, CA). The solution was held in a fluid cell and sealed

by a silicone O-ring. Prior to use, the fluid cell and the O-ring were soaked in SDS solution, rinsed with water, and dried with high-purity N₂. The sample surface was equilibrated in solution in the fluid cell for 2 h before performing imaging and lithography, in order to minimize mechanical and thermal drift. The z-axis of the piezo was calibrated by a silicon calibration reference of 22.0 nm step height (Silicon-MDT, Moscow, Russia). The x- and y-axes of the piezo were calibrated by imaging a diffraction grating replica of a 2160 lines mm⁻¹ waffle pattern (Ted Pella, Redding, CA). All measurements were performed in the temperature range 22 ± 2 °C. The force needed to produce a -COOH functionalized thiol nanoisland within the -OH functionalized SAM by nanografting was <10 nN in contact mode, while imaging was done in the tapping mode with the smallest force necessary. Contact mode images were performed at the smallest force necessary to get an image.

References

- [1] Decher G, Hong J D and Schmitt J 1992 *Thin Solid Films* **210/211** 831
- [2] For reviews, see Decher G 1997 *Science* **277** 1232
Bertrand P, Jonas A, Laschewsky A and Legras R 2000 *Macromol. Chem. Phys.* **1** 319
Hammond P T 2004 *Adv. Mater.* **16** 1271
- [3] Heflin J R, Figura C, Marciu D, Liu Y and Claus R 1999 *Appl. Phys. Lett.* **74** 495
Lvov Y, Yamada S and Kunitake T 1997 *Thin Solid Films* **300** 107–10
Heflin J R, Guzy M T, Neyman P J, Gaskins K J, Brands C, Wang Z, Gibson H W, Davis R M and Van Cott K E 2006 *Langmuir* **22** 5723
- [4] Mattoussi H, Rubner M F, Zhou F, Kumar J, Tripathy S K and Chiang L Y 2000 *Appl. Phys. Lett.* **77** 1540
Mwaura J K, Pinto M R, Witker D, Ananthakrishnan N, Schanze K S and Reynolds J R 2005 *Langmuir* **21** 10119
- [5] Delongchamp D M and Hammond P T 2001 *Adv. Mater.* **13** 1455
Jain V, Yochum H M, Montazami R and Heflin J R 2008 *Appl. Phys. Lett.* **92** 033304
- [6] Yancey S E, Zhong W, Heflin J R and Ritter A L 2006 *J. Appl. Phys.* **99** 034313
Lee D, Rubner M F and Cohen R E 2006 *Nano Lett.* **6** 2305
- [7] Clark S L and Hammond P T 2004 *Adv. Mater.* **10** 1515
- [8] Zheng H, Lee I, Rubner M F and Hammond P T 2002 *Adv. Mater.* **14** 569
- [9] Hua F, Shi J, Lvov Y and Cui T 2002 *Nano Lett.* **11** 1219
- [10] Cui T, Hua F and Lvov L 2004 *Sensors Actuators A* **114** 501
- [11] Lee S W, Sanedrin R G, Oh B and Mirkin C A 2005 *Adv. Mater.* **17** 2749
- [12] Salaita K, Wang Y and Mirkin C A 2007 *Nat. Nanotechnol.* **2** 145–55
- [13] Nyamjav D and Ivanisevic A 2004 *Chem. Mater.* **16** 5216
- [14] Yu M, Nyamjav D and Ivanisevic A 2005 *J. Mater. Chem.* **15** 649
- [15] Xu S and Liu G 1997 *Langmuir* **13** 127–9
- [16] Xu S, Miller S, Laibinis P E and Liu G-Y 1999 *Langmuir* **15** 7244
- [17] Liu G Y, Xu S and Qian Y 2000 *Acc. Chem. Res.* **33** 457
- [18] Wang Z, Heflin J R, Stolen R H and Ramachandran S 2005 *Appl. Phys. Lett.* **86** 223104
- [19] Shiratori S S and Rubner M F 2000 *Macromolecules* **33** 4213
- [20] Cruchon-Dupeyrat S, Porthun S and Liu G-Y 2000 *Appl. Surf. Sci.* **175/176** 636
- [21] Salita K, Wang Y, Fragala J, Vega R A, Liu C and Mirkin C A 2006 *Angew. Chem. Int. Edn* **45** 7220
- [22] Despont M, Drechsler U, Yu R, Pogge H B and Vettiger P 2004 *J. Microelectromech. Syst.* **13** 895
- [23] Harriott L R and Hull R 2004 *Introduction to Nanoscale Science and Technology* ed D M Ventra, S Evoy and J R Heflin (Norwell, MA: Kluwer Academic) pp 1–40
- [24] Tulpar A and Ducker W A 2004 *J. Phys. Chem. B* **108** 1667