Published in final edited form as:
J Phys Chem Lett. ; 2(14): 1804–1807. doi:10.1021/jz200749d.

Microscopic Perspective on the Adsorption Isotherm of a Heterogeneous Surface

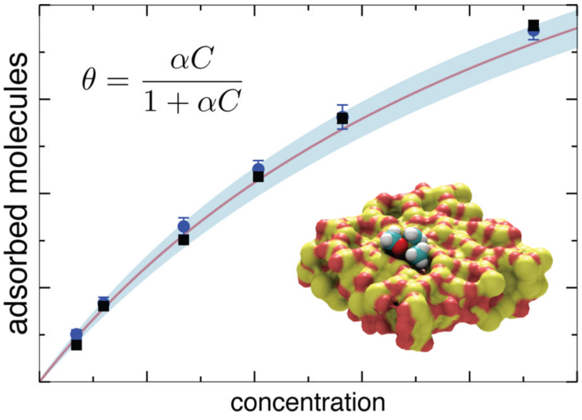
Rogan Carr[†], **Jeffrey Comer**[†], **Mark D. Ginsberg**[‡], and **Aleksei Aksimentiev**[*,¶,†]
[†]Department of Physics, University of Illinois, Urbana, IL

[‡]US Army ERDC-CERL, Champaign, IL

[¶]Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL

Abstract

Adsorption of dissolved molecules onto solid surfaces can be extremely sensitive to the atomic-scale properties of the solute and surface, causing difficulties for the design of fluidic systems in industrial, medical and technological applications. In this communication, we show that the Langmuir isotherm for adsorption of a small molecule to a realistic, heterogeneous surface can be predicted from atomic structures of the molecule and surface through molecular dynamics (MD) simulations. We highlight the method by studying the adsorption of dimethyl-methylphosphonate (DMMP) to amorphous silica substrates and show that subtle differences in the atomic-scale surface properties can have drastic effects on the Langmuir isotherm. The sensitivity of the method presented is sufficient to permit the optimization of fluidic devices and to determine fundamental design rules for controlling adsorption at the nanoscale.



Keywords

Langmuir isotherm; adsorption; nanochannel; nanofluidics; potential of mean force; molecular dynamics

Adsorption of solutes from a liquid phase to a solid substrate is a process ubiquitous across industries and technologies, yet it is often difficult to predict and control. Specific adsorption

---

[*] To whom correspondence should be addressed.

Supporting Information Available

Details of the simulation methods, setup and analysis, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org/.

has many applications, ranging from clarification in winemaking,[1] to dialysis, filtration and the treatment of acute poisoning,[2] to the purification of proteins.[3] At the same time, uncontrolled adsorption contributes to loss of product to vessel surfaces, clogging of small constrictions in coronary stents[4] or microfluidic devices[5] and performance deterioration of biosensors.[6,7] The microscopic nature of adsorption phenomena requires the atomic structures of the solutes and the substrates be taken into account in order to design substrates to have set adsorption properties for specific solutes. In this communication, we describe a computational method for prediction of the adsorption isotherm specific to the atomic-scale details of the solute, solvent and substrate. Building on previous work in this area,[7–14] we demonstrate utility of classical molecular dynamics (MD) simulations for prediction of macroscopic, experimentally accessible adsorption behavior of realistic, heterogeneous surfaces.

Monolayer adsorption is commonly described by the Langmuir isotherm

$$\theta=\frac{\alpha C_{\mathrm{bulk}}}{1+\alpha C_{\mathrm{bulk}}}, \tag{1}$$

where θ is the fractional area of the surface covered by the adsorbed solutes, C_{bulk} is the solutes' bulk concentration and the empirical parameter α specifies the solute–surface affinity, also known as the Langmuir constant. For a homogeneous surface containing a lattice of identical binding sites that can be occupied by only one solute, the Langmuir description is exact, with a being equal to the inverse of the bulk concentration at which half the surface is covered with the solute. In practice, most surfaces are neither periodic nor homogeneous in their binding affinity, and hence the Langmuir constant α is determined from experiment. Below we demonstrate that, in the case of a realistic heterogeneous surface, the Langmuir isotherm can be directly obtained from MD simulations and the Langmuir constant α can be computed from a 3-dimensional potential of mean force (3D PMF) for the solute near the surface.

To simulate surface adsorption in all-atom detail, we have modeled a small, enclosed chamber of solution, using dimethyl methylphosphonate (DMMP) as a model solute. Figure 1 (top) shows a typical starting configuration of a simulation system consisting of a 10 × 10 nm^2 slab of amorphous silica (SiO_2), tiled from sixteen identical 2.5 × 2.5 nm^2 patches, enclosing a 5–6 nm tall, well-mixed aqueous solution of DMMP. The system was made effectively infinite in the $x-y$ plane using the periodic boundary conditions. A pressure gradient was imposed in one of the directions, producing a Poiseuille-type flow.[15] The magnitude of the flow had negligible effect on adsorption. A complete description of the system setup and the simulation protocols is provided in Supporting Information.

After initial energy minimization and equilibration, the system was simulated for ~100 ns using the classical MD method.[16] As the simulation progressed, the concentration of DMMP in the center of the chamber gradually reduced as DMMP adsorbed to the surfaces of the slab. Figure S1 in the Supporting Information plots the number of adsorbed molecule versus time in a typical simulation. In less than 100 ns, the systems reach a dynamic equilibrium state, Figure 1 (bottom), which we used to calculate the average density of adsorbed solutes n and the bulk concentration C_{bulk}, different from the starting concentration. Here we defined a solute as adsorbed at the surface if its center of mass lies within 0.5 nm of the surface. As detailed in Figure 1, the equilibrium profile of DMMP concentration exhibits pronounced maxima near both surfaces of the slab and is constant elsewhere, and hence we refer to these two regions as the adsorption layer and bulk solution, respectively.

To obtain the adsorption isotherm, we repeated the above simulation having different starting amounts of DMMP in the chamber. The resulting dependence of the density of adsorbed solutes on the bulk concentration is shown in Figure 2 (black squares) along with the fit of the data to the Langmuir isoterm, Eq. (1) (solid line). The plot shows that the simulated adsorption obeys the Langmuir isotherm. To extract the Langmuir constant, independent MD simulations were performed to determine n_{max}—the maximum adsorption density of DMMP, which is required to compute the fractional surface coverage θ using the adsorption surface density n as $\theta = n/n_{\text{max}}$ (see Supporting Figure S2).

Thus, we have shown the utility of brute-force MD for predicting the Langmuir constant of a heterogeneous surface. Being essentially the numerical equivalent of an actual experiment, such an approach may not be optimal for designing surfaces with set adsorption properties, as it would require a large number of trials.

To link the local atomic-scale properties of the substrate and the solvent to the global adsorption properties of the surface, we express the Langmuir isotherm in terms of microscopic quantities. For a low-concentration solution, the Langmuir isotherm, Eq. (1) reduces to

$$\theta=\alpha\cdot C_{\text{bulk}}, \tag{2}$$

and the concentration near the surface can be obtained as

$$C(\vec{r})=C_{\text{bulk}}e^{-F(\vec{r})/k_{\text{B}}T}, \tag{3}$$

where $F(\vec{r})$ is the free energy for a solute at position $\vec{r}$, set to zero in the bulk. By integrating the solute concentration over the adsorption layer (Figure 1) and dividing by the area of the surface, A_{surface}, the density of molecules adsorbed at the surface is

$$n=\frac{C_{\text{bulk}}}{A_{\text{surface}}}\int_{\text{adsorbed}}d\vec{r}\,e^{-\beta F(\vec{r})}. \tag{4}$$

Using $\theta = n/n_{\text{max}}$, we find $n = \alpha\cdot C_{\text{bulk}}\cdot n_{\text{max}}$, or

$$\alpha\cdot C_{\text{bulk}}\cdot n_{\text{max}}=\frac{C_{\text{bulk}}}{A_{\text{surface}}}\int_{\text{adsorbed}}d\vec{r}\,e^{-\beta F(\vec{r})} \tag{5}$$

$$\alpha=\frac{1}{n_{\text{max}}\cdot A_{\text{surface}}}\int_{\text{adsorbed}}d\vec{r}\,e^{-\beta F(\vec{r})}, \tag{6}$$

which expresses the Langmuir constant α in terms of the maximum adsorption density n_{max} and the free energy $F(\vec{r})$. In this expression, n_{max} contains the information about the high-concentration behavior of the system.

To determine the free energy of a solute as a function of its position near the surface, we performed umbrella-sampling simulations[17] of DMMP and the silica slab and obtained the 3D PMF using the weighted histogram method (WHAM)[18] generalized to three dimensions (see Supporting Information). Such 3D PMF maps can be thought of as the change in free energy for bringing the solute molecule from the bulk solution to any point near the surface and reveals the variation in adsorption strength over the surface.

Figure 3 illustrates the results of such calculations, showing the silica surface colored by the local minimum value of the PMF for each (x,y) point. For this particular 2.5 × 2.5 nm^2 patch of amorphous silica surface, the depth of the PMF near the surface varies from 0 to −6.6 k_BT. The surface appears to have low and high affinity regions, highlighting its heterogeneous nature. The inset in Figure 3 shows the PMF as a function of z, averaged over the $x - y$ plane, revealing the short-range nature of the interaction. The shape of the average PMF is in accord with the steady-state concentration profile of DMMP in Figure 1.

Using Eq. (3), we have computed the Langmuir constant from the 3D PMF map shown in Figure 3 and the previously-determined maximum adsorption density n_{max}. The value predicted by the 3D PMF model: $\alpha_{Model} = 2.0 \pm 0.1$ M^{-1}, is in excellent agreement with the fit to the adsorption simulation data: $\alpha_{Fit} = 1.9 \pm 0.2$ M^{-1}, where the errors were estimated taking into account the uncertainty of determining n_{max} and the 3D PMF, or the surface concentration in the brute force MD data, respectively. Consequently, adsorption densities predicted by the model agree with the results of brute-force MD in the entire range of studied concentrations, Figure 2. Our model also describes the high-concentration regime for which n_{max} was determined. For example, at 4.6 M the Langmuir model predicts the adsorption density of 1.4 ± 0.12 nm^{-2}, which is within the error of the brute-force MD value of 1.55 ± 0.01 nm^{-2}.

To test the robustness of the 3D PMF model against variations in the atomic-scale features of the substrate surface, we repeated both brute-force and 3D PMF calculations for three additional amorphous silica slabs that had different surface features introduced by thermal annealing[8] (see Supporting Information). Figure 4 (a–d) illustrate the atomic structures of the four surfaces; data presented in Figures 1, 2 and 3 pertain to surface A. Surface B was simulated in a chamber constructed using both surface A and B, with surface A on the bottom and B on the top, which is referred to as system AB. For comparison, the same calculations were performed for a frictionless hydrophobic surface[19] (Ph) devoid of any atomic-scale features.

Figure 4 e compares the predictions of the 3D PMF model with the results of the brute-force MD simulations. In all cases, the two models produced quantitatively consistent results. Because of the considerable difference in the overall affinity of the surfaces to DMMP, to make the comparison statistically significant, lower-affinity systems were simulated at higher bulk concentrations of the solute.

In Eq. (3), n_{max} is assumed to be a constant global property of the surface, an assumption that may not hold for extremely heterogeneous or patterned surfaces. In these cases, constant n_{max} may still approximate large subsections of the surface and the global adsorption can be determined as a weighted average over the constant n_{max} subsections. Results for system AB illustrate this point. In Figure 4, data points A_{AB} and B_{AB} show the predicted and simulated adsorption density on only surface A and B, respectively; AB shows the total on both surfaces.

The Langmuir constants of the four silica surfaces are plotted in Figure 5. Surprisingly, we find that subtle variations in the arrangement of the surface atoms (see Figure 4 (a–d)) can alter the Langmuir constant by three orders of magnitude. To determine the microscopic cause for such an effect, we have computed local maps of the atomic scale roughness and the surface charge density for each surface and compared the resulting 2D plots with the 2D plot of the PMF's local minima, see Supporting Information Figure S3. Whereas some correlation between the surface topography and the PMF maps is apparent (see the right-most column in Figure S3), there is no consistent dependence, as indicated by the plot of the Langmuir constant versus the root mean squared (RMS) roughness of the surfaces, Figure S4. Similarly, neither the local pattern of the surface charges correlate with the PMF maps nor does the global surface charge with the Langmuir constant, see Figure S5.

Nevertheless, Figure 5 (a) shows a strong anticorrelation between the Langmuir constant and the RMS surface charge, suggesting a hydrophobic effect in the mechanism of DMMP attraction to silica. Indeed, it was previously shown that an amorphous silica surface becomes more hydrophobic as the number of dangling atoms (responsible for the high RMS charge density) is reduced.[8] The annealing procedure used to create the silica surfaces has exactly that effect. Inspection of the DMMP conformation in the bound state confirms this assertion: on average, the P–O bond of DMMP was found to point away from the surface, exposing the oxygen to the solution. As shown in Figure 5 b, surfaces that exhibit stronger adsorption of DMMP also produce a stronger orientational order. As the phantom surface, a neutral barrier with no atoms, has a smaller Langmuir constant than any of the silica surfaces, the adsorption of DMMP to silica is not primarily driven to minimize water-DMMP contacts, but rather to exclude water from hydrophobic patches of silica. Here, the local properties of the solution clearly play an important role, as they are known to depend on the atomic-scale features of the surface.[20,21]

In this letter, we have described and validated a computational method for predicting the Langmuir adsorption isotherm of realistic heterogeneous surfaces. The method permits macroscopically observable properties to be directly related to the atomic structure of the solute, solvent and the substrate and can be applied to study adsorption of any small, weakly interacting solutes and broad range of surfaces, including metals, oxides, polymers, and functionalized and patterned substrates, provided the solute-substrate interactions are appropriately described.[22,23] The exquisite sensitivity of the method to the atomic-scale features of the systems will find practical application in rational design of surfaces to minimize non-specific adsorption, maximize selective binding of desired solutes, and determine fundamental design rules that govern adsorption at the nanoscale.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The authors would like to thank Karin Dahmen and Vincent Hock for their comments on this work. This work was supported by grants from the National Science Foundation (DMR-0955959), the Petroleum Research Fund (48352-G6) and through a cooperative research agreement with the U.S. Army Engineer Research and Development Center - Construction Engineering Research Laboratory (ERDC-CERL). The authors gladly acknowledge supercomputer time provided by the TeraGrid through grant MCA05S028 and through the Department of Defense High Performance Computing Modernization Program at the ERDC Supercomputing Resource Center, Vicksburg, Mississippi.

References

1. Castellari M, Versari A, Fabiani A, Parpinello G, Galassi S. Removal of Ochratoxin A in Red Wines by Means of Adsorption Treatments with Commercial Fining Agents. J. Agric. Food Chem. 2001; 49:3917–3921. [PubMed: 11513689]
2. Mikhalovsky S. Emerging Technologies in Extracorporeal Treatment: Focus on Adsorption. Perfusion. 2003; 18:47–54. [PubMed: 12708765]
3. Regnier F, Gooding K. High-Performance Liquid Chromatography of Proteins. Anal. Biochem. 1980; 103:1–25. [PubMed: 6990825]
4. Thierry B, Merhi Y, Bilodeau L, Trepanier C, Tabrizian M. Nitinol Versus Stainless Steel Stents: Acute Thrombogenicity Study in an Ex Vivo Porcine Model. Biomaterials. 2002; 23:2997–3005. [PubMed: 12069342]
5. Tegenfeldt JO, Prinz C, Cao H, Huang RL, Austin RH, Chou SY, Cox EC, Sturm JC. Micro- and Nanofluidics for DNA Analysis. Anal. Bioanal. Chem. 2004; 378:1678–1692. [PubMed: 15007591]

6. Niedzwiecki DJ, Grazul J, Movileanu L. Single-Molecule Observation of Protein Adsorption onto an Inorganic Surface. J. Am. Chem. Soc. 2010; 132:10816–10822. [PubMed: 20681715]

7. Radadia AD, Stavis CJ, Carr R, Zeng H, King WP, Carlisle JA, Aksimentiev A, Hamers RJ, Bashir R. Control of Nanoscale Environment to Improve Stability of Immobilized Proteins on Diamond Surfaces. Adv. Funct. Mater. 2011; 21:1040–1050. [PubMed: 21949497]

8. Cruz-Chu ER, Aksimentiev A, Schulten K. Water-Silica Force Field for Simulating Nanodevices. J. Phys. Chem. B. 2006; 110:21497–21508. [PubMed: 17064100]

9. Hassanali AA, Singer SJ. Model for the Water–Amorphous Silica Interface: The Undissociated Surface. J. Phys. Chem. B. 2007; 111:11181–11193. [PubMed: 17803296]

10. Park J, Aluru N. Temperature-Dependent Wettability on a Titanium Dioxide Surface. Mol. Sim. 2009; 35:31–37.

11. Schneider J, Ciacchi LC. A Classical Potential to Model the Adsorption of Biological Molecules on Oxidized Titanium Surfaces. J. Chem. Theory Comput. 2011; 7:473–484.

12. Wang B, Kral P. Optimal Atomistic Modifications of Material Surfaces: Design of Selective Nesting Sites for Biomolecules. Small. 2007; 3:580–584. [PubMed: 17328013]

13. Serr A, Horinek D, Netz R. Polypeptide Friction and Adhesion on Hydrophobic and Hydrophilic Surfaces: A Molecular Dynamics Case Study. J. Am. Chem. Soc. 2008; 130:12408–12413. [PubMed: 18712864]

14. Ziemys A, Ferrari M, Cavasotto C. Molecular Modeling of Glucose Diffusivity in Silica Nanochannels. J Nanosci. Nanotechnol. 2009; 9:6349–6359. [PubMed: 19908533]

15. Carr R, Comer J, Ginsberg MD, Aksimentiev A. Modeling Pressure-Driven Transport of Proteins through a Nanochannel. IEEE Tran. Nanotechnol. 2011; 10:75–82.

16. Phillips JC, Braun R, Wang W, Gumbart J, Tajkhorshid E, Villa E, Chipot C, Skeel RD, Kale L, Schulten K. Scalable Molecular Dynamics with NAMD. J. Comp. Chem. 2005; 26:1781–1802. [PubMed: 16222654]

17. Torrie G, Valleau J. Nonphysical Sampling Distributions in Monte Carlo Free-Energy Estimation: Umbrella Sampling. J. Comp. Phys. 1977; 23:187–199.

18. Roux B. The Calculation of the Potential of Mean Force Using Computer Simulations. Comp. Phys. Comm. 1995; 91:275–282.

19. Heng JB, Aksimentiev A, Ho C, Marks P, Grinkova YV, Sligar S, Schulten K, Timp G. The Electromechanics of DNA in a Synthetic Nanopore. Biophys. J. 2006; 90:1098–1106. [PubMed: 16284270]

20. Sendner C, Horinek D, Bocquet L, Netz RR. Interfacial Water at Hydrophobic and Hydrophilic Surfaces: Slip, Viscosity, and Diffusion. Langmuir. 2009; 25:10768–10781. [PubMed: 19591481]

21. Poissier A, Ganeshan S, Fernandez-Serra MV. The Role of Hydrogen Bonding in Water- Metal Interactions. Phys. Chem. Chem. Phys. 2011; 13:3375–3384. [PubMed: 21180721]

22. Ghiringhelli L, Hess B, van der Vegt N, Delle Site L. Competing Adsorption Between Hydrated Peptides and Water onto Metal Surfaces: From Electronic to Conformational Properties. J. Am. Chem. Soc. 2008; 130:13460–13464. [PubMed: 18788811]

23. Dianat A, Seriani N, Ciacchi L, Pompe W, Cuniberti G, Bobeth M. Dissociative Adsorption of Methane on Surface Oxide Structures of Pd–Pt Alloys. J. Phys. Chem. C. 2009; 113:21097–21105.

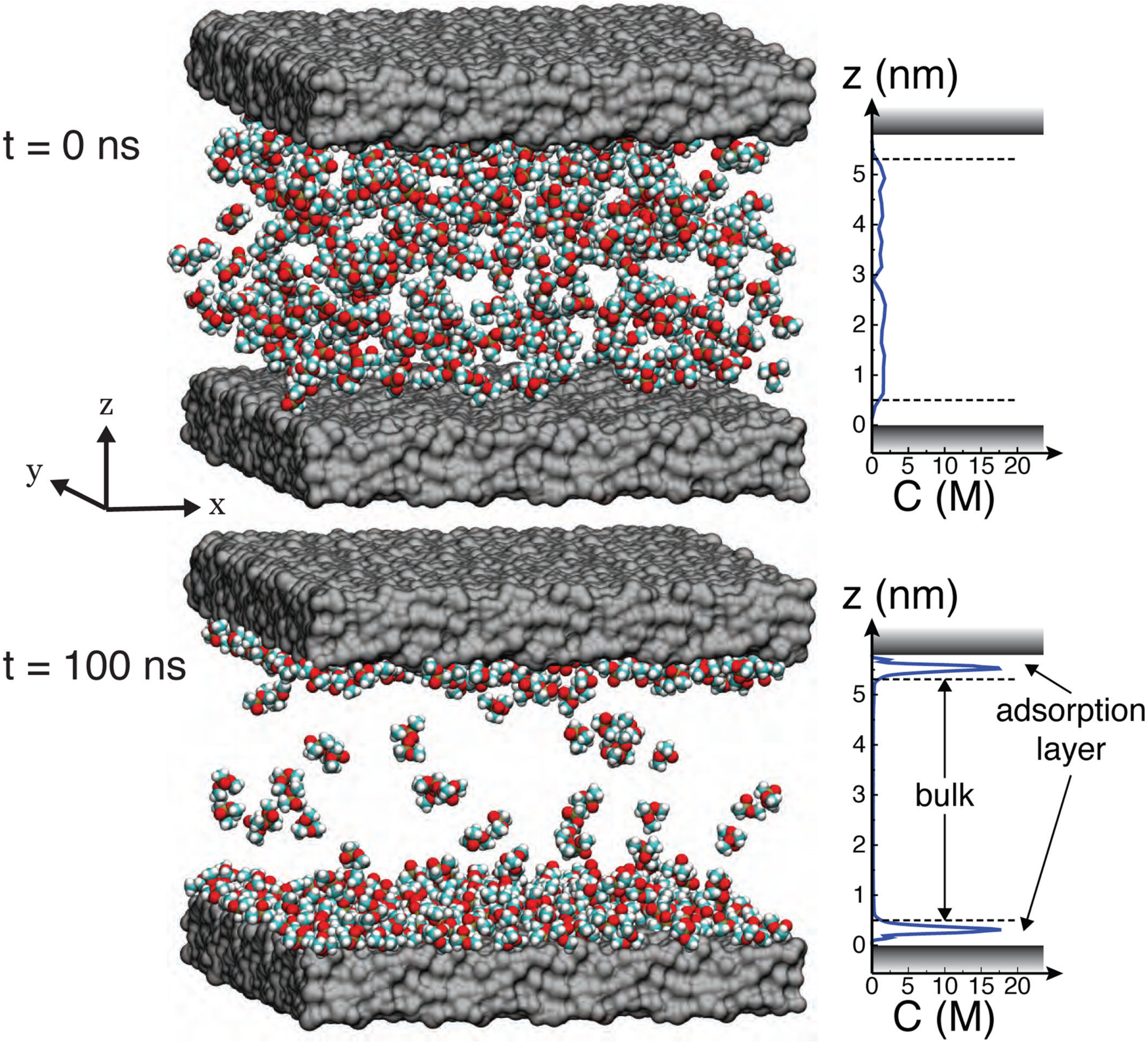


Figure 1.

Molecular dynamics simulations of adsorption. (Top) Typical starting configuration containing randomly placed DMMP solute (shown as vdW spheres), two silica slabs (shown as gray molecular surfaces) and water (not shown). The plot specifies the average concentration of the solute along the *z* axis. (Bottom) The same system at the end of a 100-ns MD trajectory.

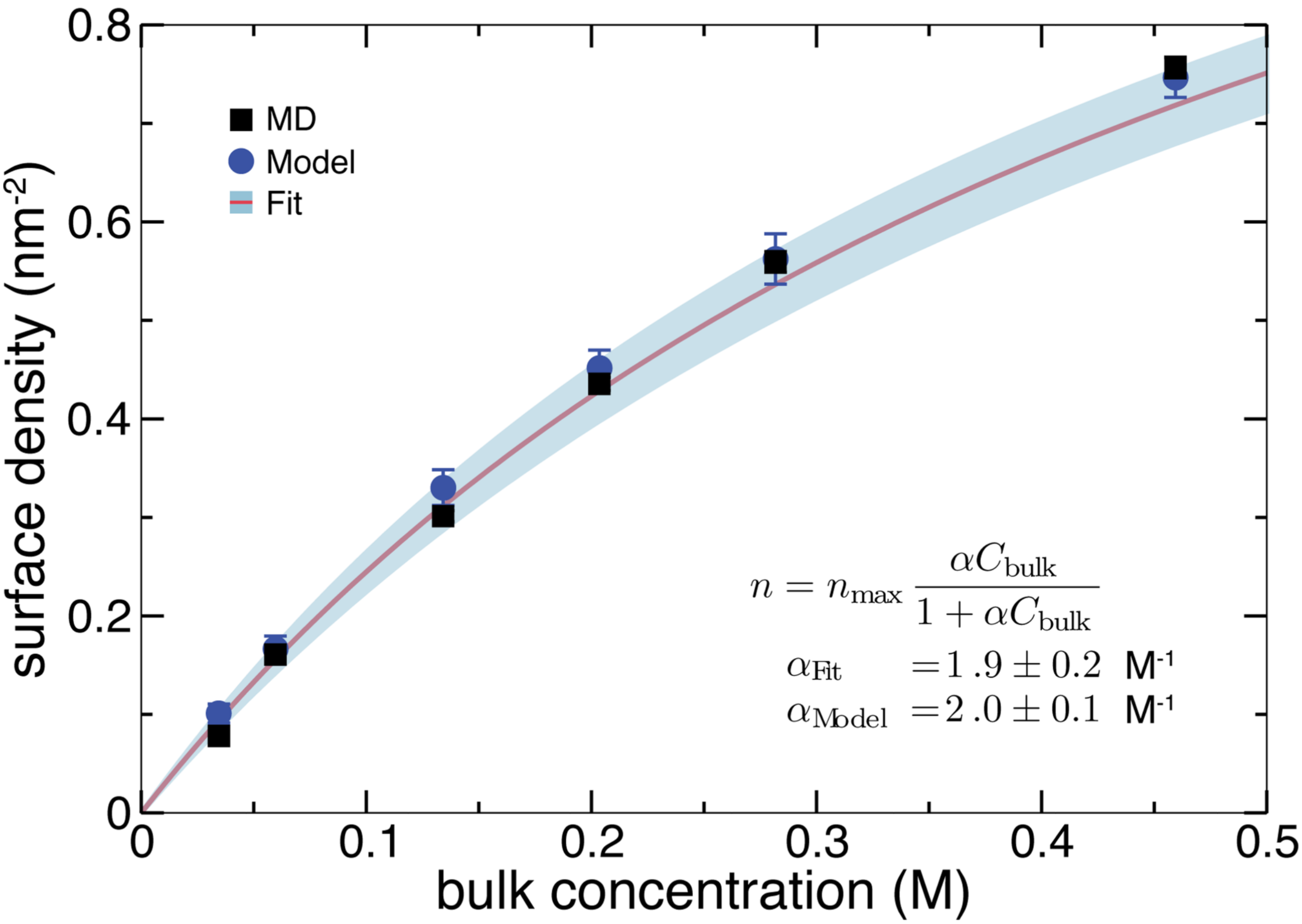


Figure 2.

Adsorption isotherm. Black squares indicate the data directly obtained from all-atom MD simulations. The solid line shows the fit of the Langmuir isotherm to the MD data; the expected error of the fit is shown in light blue. Blue circles show the predictions of the theoretical model based on the 3-dimensional potential of mean force (see text).

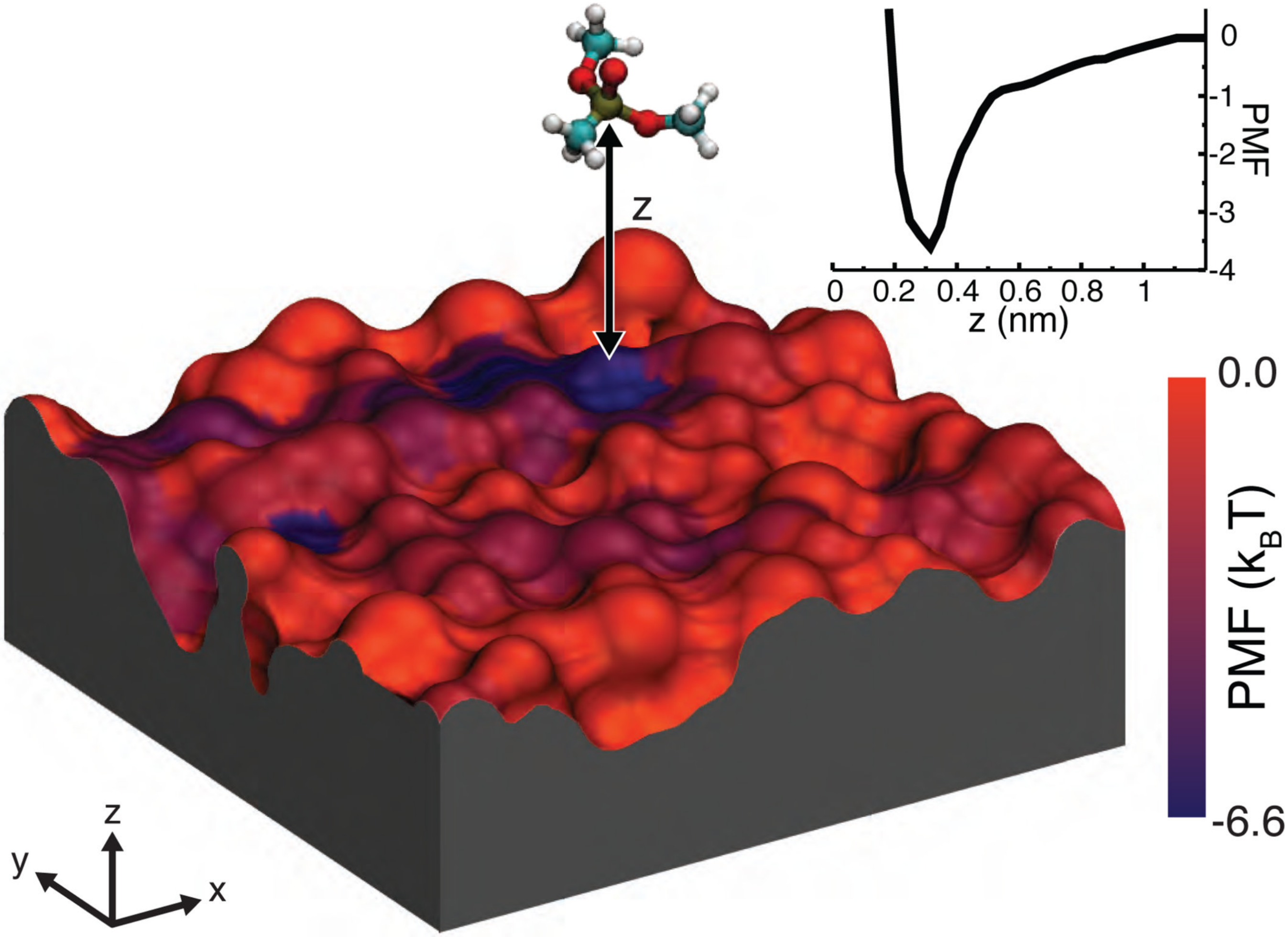


Figure 3.

Potential of mean force (PMF) of a DMMP solute in proximity to a heterogeneous surface. The silica slab is shown as a molecular surface colored by the local minimum value of the PMF in the direction normal to the slab (see text). Inset shows the PMF averaged over the x–y plane as a function of the distance from the surface.

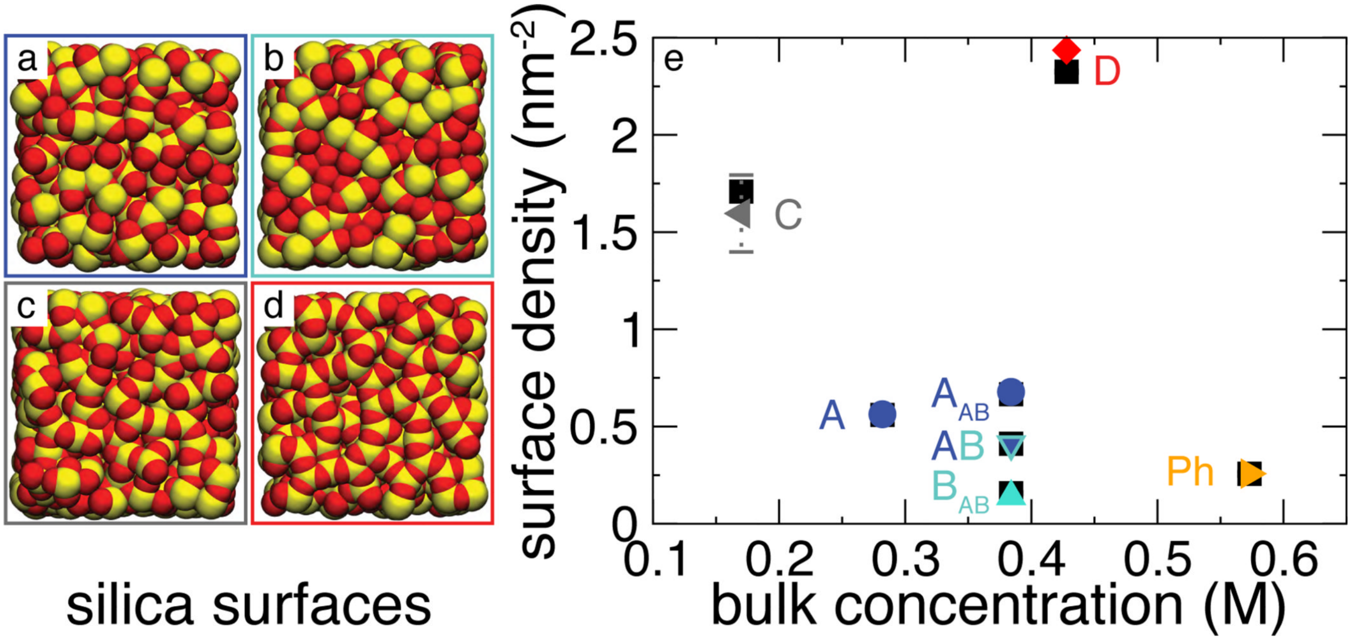


Figure 4.

Test of the 3D-PMF model of adsorption using different heterogeneous surfaces. (a–d) Atomic model of the surface of silica slabs A–D, respectively. Oxygen and silicon atoms are shown as red and yellow vdW spheres, respectively. (e) Test of the model. Black squares indicate data directly obtained from MD simulations, other symbols show predictions of the 3D-PMF model. Labels A, B, C, and D indicate the surfaces the data were obtained for (also shown as panels a–d); AB labels the system that combined two different surfaces (A and B, labeled A_{AB} and B_{AB}), and Ph indicates a phantom surface, a smooth surface that lacks atomic-scale features (see text).

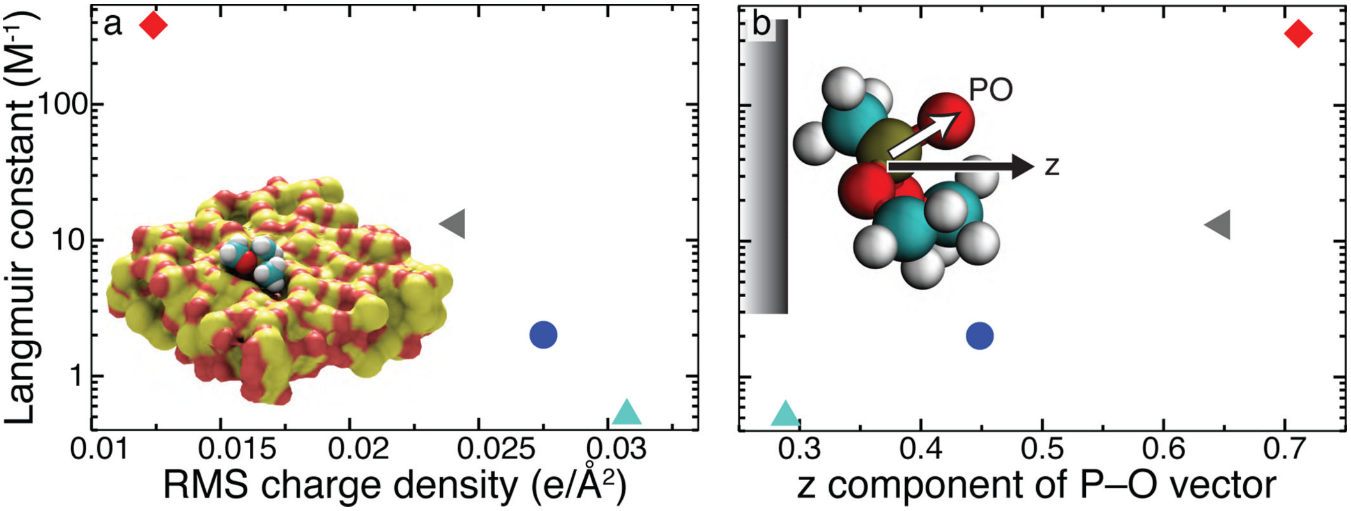


Figure 5.

Atomic features affect adsorption. For the four silica surfaces, the Langmuir constant is plotted as a function of (a) the root mean square (RMS) surface charge density and (b) the conformation of the adsorbed solutes. The latter is characterized by the average projection of the P–O bond unit vector onto the normal of the slab. Colors and symbols are the same as in Figure 4 e. Inset to (a) shows a DMMP molecule bound to a small pocket (surface D).