THE JOURNAL OF PHYSICAL CHEMISTRY A-

Linear Response Theory for Water Transport Through Dry Nanopores

Published as part of The Journal of Physical Chemistry virtual special issue "Veronica Vaida Festschrift".

Steven E. Strong[®] and Joel D. Eaves^{*®}

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, United States

ABSTRACT: Porous two-dimensional crystals like graphene have the potential to revolutionize reverse-osmosis membrane technology. The permeability is a common figure of merit that describes the ease with which water flows through a membrane. For two-dimensional crystals, the permeability can be orders of magnitude higher than it is in conventional reverse-osmosis membranes. We apply our Gaussian Dynamics nonequilibrium molecular dynamics simulation method to very hydrophobic two-dimensional membranes and find that the current—pressure drop relationship becomes nonlinear. In this regime, the conventional permeability is an inadequate descriptor of the passage process, and the transport mechanism becomes a twostep one. The backing pressure first causes the pore to wet, and



after it reaches a threshold pressure, water transport takes place from the wet state. We recover a simple description of the transport process by applying linear response theory with respect to the wet reference state rather than the dry one. A macroscopic thermodynamic argument supports our mechanistic description and predicts the wetting threshold pressure as a function of the contact angle.

INTRODUCTION

Veronica Vaida appreciates the power of simple pictures, particularly when it comes to the basic physical chemistry of water and aqueous solution-phase chemistry. In a seminal paper, she and collaborators argued that a combination of thermodynamic and hydrodynamic phenomena could produce prebiotic aqueous "containers," coated in an organic layer and roughly the size of a modern cell.¹ The interplay between the hydrophobic effect of small organic molecules and the evaporation, condensation, division, and coagulation of these containers dictates their size and composition distribution. The authors hypothesized that such containers played a pivotal role in the origin of life by concentrating, exchanging, and protecting the precursors to biochemistry. This hypothesis is a compelling one that several other groups have subsequently explored.^{2–7}

Similar in spirit to the work of ref 1, we advance a basic thermodynamic line of attack to explain a hydrophobic effect in a very different system. We focus on the aqueous transport dynamics of porous two-dimensional crystals. These materials hold great promise for next-generation water desalination membranes. Because they are atomically thin, the membrane permeability, which is proportional to the water current per unit applied pressure, is predicted to be two to three orders of magnitude higher than that of a conventional membrane.^{8–13} In these systems a natural question arises: is it better to have a hydrophobic membrane or a hydrophilic one for reverse osmosis (RO)? In previous publications, we found that the

answer to such a simple conceptual question was complicated. $^{12,13} \,$

To summarize our previous work, the hydrophobic contact angle is an incomplete predictor of a two-dimensional membrane's permeability. Both polar and van der Waals interactions are distinct forms of intermolecular interactions, but each type has a profoundly different impact on how water moves through pores in a two-dimensional crystal. By charging a two-dimensional sheet through doping, the sheet becomes more hydrophilic through a completely collective effect called electrowetting.¹⁴ But when molecules pass through pores in a charged sheet, they are most sensitive to the local electrostatic potential from the atoms in the vicinity of the pore.¹¹ Chemically terminating a pore with electron-withdrawing groups allows the hydrogen atoms in the water molecules to rotate about the massive oxygen atom and form primary contacts with the sheet.¹³ When the pore is negatively charged, it is easier for water molecules to give up hydrogen bonds as they cross the sheet. In contrast to the completely collective hydrophobic effect from electrowetting, this asymmetry between hydrogen bond donation and acceptance is a molecular-scale phenomenon.

The impact of the van der Waals interactions is more subtle. For changes in the depth of the van der Waals potential by fractions of $k_{\rm B}T$, the wetting contact angle, and therefore the

Received:
 April 4, 2017

 Revised:
 June 7, 2017

 Published:
 June 9, 2017

hydrophobicity, changes dramatically.¹⁵ As the sheet becomes more hydrophobic, the pore gains thermodynamic stability by spontaneously expelling the water molecules from it and drying.¹³ The competition between the statics of dewetting and hydrodynamic friction determines the optimal contact angle.¹³

The thermodynamic agreement appearing in ref 13 for the optimal contact angle seems specious. As in the system addressed by Vaida and co-workers,¹ the system we studied is not at equilibrium. But even more troubling is that we distinguish between a vapor and liquid phase in the pore by the occupancy of two or three water molecules. The molecular dimensions of this system make the dry and wet states metastable so that the fluctuations between them are facile. Were they not, the dry state would be unable to transport water. In this paper, we sharpen our original thermodynamic framework to show that bulk, equilibrium thermodynamics does give semiquantitative insights into this system.

The permeability is related to a transport coefficient and can therefore be computed using linear response theory. Linear response theory uses the natural fluctuations around an equilibrium reference state to describe how a system behaves away from equilibrium, and is at the heart of nonequilibrium statistical mechanics.^{16,17} For the least permeable sheets, the pressure differential is so large that the system could be pushed into the nonlinear regime (Figure 1). If one regards the



Figure 1. On a hydrophobic (contact angle, $\theta = 128^{\circ}$) double-layer atomic membrane, the relationship between the current and the pressure drop is not linear with zero intercept. The black points show the results from 192 Gaussian dynamics simulations. Naively applying eq 1 to compute the permeability by fitting yields the conventional permeability (blue). The orange line shows an example of a nonlinear description for the relationship that fits both the data and the equilibrium system that necessarily has zero current and zero pressure drop.

permeability as the hydrodynamic analogue of electrical conductivity, where voltage plays the role of the pressure differential, the current-pressure drop $(q-\Delta P)$ relationship sketched in Figure 1 looks like the current-voltage characteristic of a diode, which is clearly nonlinear.¹⁸ In this paper, we turn again to thermodynamics to show that such an apparently nonlinear relationship can be made to obey linear response in the right reference state.¹⁹

METHODS

We study the flow of water through atomically thin porous membranes that are inspired by nanoporous double-layer graphene. They have the same geometry as double-layer graphene and their hydrophobicity is a function of the Lennard-Jones ϵ parameter for the water-membrane atom interac-tion.^{13,15} The wetting contact angle θ quantifies the hydro-phobicity.^{13–15} All simulation methods are the same as those reported in ref 13. Some simulations here are 5 ns longer to ensure that they are at steady state, so some permeabilities reported here are slightly different from ref 13. It is easiest to compute the permeability quantity away from equilibrium, using Gaussian dynamics to hold the current fixed, as described in our previous references.^{12,13} Permeabilities computed using Gaussian dynamics average more quickly than those deduced from linear response theories of equilibrium fluctuations, and Gaussian dynamics is not limited to near equilibrium transport. The permeability is proportional to the slope of the $q-\Delta P$ relationship^{12,13,2}

$$p \equiv k_{\rm B} T \left(\frac{q}{\Delta P} \right) \tag{1}$$

where ΔP is the pressure drop across the membrane, *q* is the current of water through the pore expressed in molecules per unit time, *T* is the temperature, and $k_{\rm B}$ is Boltzmann's constant.

RESULTS AND DISCUSSION

Increasing the contact angle from approximately 30°, the permeability of an atomically thin membrane increases monotonically until the dewetting transition, where the channel dries and the permeability decreases abruptly.¹³ The terms dry and wet state are anecdotal, because in molecular scale systems like these, spontaneous transient fluctuations between the binary states do occur. The maximum permeability occurs near the critical dewetting contact angle, which depends on the channel geometry, particularly the aspect ratio.¹³ As the pore becomes drier, fluctuations into the wet state become more rare, and a larger applied pressure drop is required to induce the fluctuations into the wet state that allow transport. This pressure drop forces the system far from the equilibrium state, possibly into the nonlinear $q - \Delta P$ regime (Figure 1). Were such a nonlinear description accurate, one would need to abandon basic linear response theory and describe the transport process with a differential permeability.

Linear response relies on the notion that a system that is fluctuating about a stable reference state cannot distinguish between an equilibrium fluctuation and a small external perturbation. Under the action of a generalized force f the nonequilibrium average \overline{A} is linear in f

$$\overline{A} = \langle A \rangle_{\text{ref}} + \chi_{\text{ref}} f \tag{2}$$

where $\langle \cdot \rangle_{\text{ref}}$ is an average in the reference (unperturbed) ensemble, and χ_{ref} is the susceptibility computed in the reference state. In the context of this paper, the observable is the current $A \equiv q$, and the force is the applied pressure drop $f \equiv \Delta P$. For a very hydrophobic membrane, the reference state is ambiguous. Both wet and dry states are dynamically metastable and the transitions between them become more frequent as ΔP increases toward the wetting pressure. An alternative to the nonlinear description of the $q-\Delta P$ relationship sketched in Figure 1 is a two-step process for passage in



Figure 2. On hydrophobic membranes, past the dewetting transition, fluctuations into the wet state are rare, but a large enough applied pressure drop ΔP wets the pore and allows passage.

which the pore must first wet under a large applied pressure drop ΔP before passage can occur (Figure 2).

In the simplest possible manifestation of this two-step process, the transport is still in the linear regime after the initial wetting step. We apply this model to our nonequilibrium $q-\Delta P$ data by fitting the $q-\Delta P$ relationship to a line with nonzero intercept (Figure 3a). We call the slope of this line the "wet permeability", because it is equivalent to the linear response permeability computed with respect to the wet reference state. Below the dewetting transition, the wet permeabilities match those from ref 13, as they should, since there is no dry state (Figure 3b). The small differences between the wet and conventional permeabilities here are simply due to errors in the fitting process. At the dewetting transition, the wet permeability decreases along with the conventional permeability but then increases past the transition.

In the conventional picture, the $q - \Delta P$ relationship is completely specified by a single parameter, the slope or permeability (eq 1). The conventional permeability fundamentally cannot capture a nonlinear $q - \Delta P$ relationship, because, like a differential resistance, it depends on the range of values of *q* sampled in the simulations. For simulations that use the same values of q as in refs 12 and 13, the conventional permeability can still give a qualitative picture, in which increased resistance to passage results in a lower permeability, but it does not give the whole picture. An accurate description of the transport must recognize that it is a two-step process. This two-step process is described by two parameters instead of one, the threshold pressure $\Delta P_{\rm T}$, which is the intercept on the abscissa in Figure 3a, and the slope past $\Delta P_{\rm T}$. The slope is related to the permeability in the usual way, and $\Delta P_{\rm T}$ is the pressure threshold for wetting the pore away from equilibrium.

We compute the pressure threshold from the intercept of the linear fit to the nonequilibrium $q - \Delta P$ data (Figure 3a). The pressure threshold is roughly zero below the dewetting transition, as expected, and then increases past it (Figure 4a). From a practical RO perspective, the wet permeabilities shown in Figure 3a imply that a very hydrophobic membrane ($\theta \approx$ 140°) is almost as permeable as the optimal membrane with θ $\approx 80^{\circ}$. This is misleading, however, because the performance of an RO device depends on the entire $q-\Delta P$ relationship, not just its slope. For an RO facility to take advantage of the high permeability of hydrophobic membranes, it would need to operate at applied pressures above the wetting pressure of the pores, which is clearly not feasible (Figure 4a). Note that the fluctuations in the pressure threshold peak at the dewetting transition, analogous to the susceptibility at a second-order phase transition (Figure 4a).



Figure 3. (a) On hydrophobic ($\theta = 128^{\circ}$) double-layer atomic membranes, the relationship between the current and the pressure drop is not linear with zero intercept. We fit the results from 192 Gaussian dynamics simulations (black) to lines with zero (blue) and nonzero intercept (orange). The orange line describes a two-step process for passage (see the text). The pore first wets under a large applied pressure drop (orange "dry" segment), and then passage occurs with the usual linear $q-\Delta P$ relationship ("wet permeability"). The shaded regions show the standard error on the fits. (b) The slope of the blue line in (a) gives the conventional permeabilities from ref 13 (eq 1), while the slope of the orange line gives the wet permeability. The wet permeability follows the same trend as the conventional permeability below the dewetting transition, as it should, but above the dewetting transition, it increases.

Equilibrium simulations at varying pressures show that the nonequilibrium pressure threshold roughly corresponds to the equilibrium wetting pressure of the pore (Figure 4b). At 1 atm, a hydrophobic membrane is in a dry state at equilibrium, and the pore is most likely empty. As the external pressure increases, the peak in the pore occupation distribution shifts to three molecules, which corresponds to the wet state seen on hydrophilic membranes (Figure 4b). In these finite systems, where the difference between the wet and dry states depends on the occupation of three molecules, the dewetting transition is far from sharp. This makes it difficult to specify a precise equilibrium wetting pressure, but the equilibrium wetting pressures are on the order of 100s of MPa, similar to the nonequilibrium pressure thresholds (Figure 4a). The pressure intercept of the $q - \Delta P$ relationship is a nonequilibrium pressure threshold for wetting the pore. It is an upper bound for the true equilibrium wetting pressure. The two are equal only when the transport process is reversible. Note that the occupation probabilities in Figure 4b are more broad than Poisson



Figure 4. (a) The pressure threshold for a double-layer atomic membrane as a function of the contact angle computed from the intercept of the $q-\Delta P$ relationship along the abscissa in Figure 3a. At the dewetting transition, this pressure threshold becomes nonzero. (b) The number of water molecules in the pore region as a function of the pressure at equilibrium. The pore region is defined in ref 13 and shown in light blue in Figure 5c. At 1 atm (0.1 MPa), the hydrophobic membrane ($\theta = 128^\circ$, solid black) is dry and the hydrophilic membrane ($\theta = 29^\circ$, dotted black) is wet. Increasing the external pressure wets the hydrophobic pore (purple and green). While the dewetting transition is not sharp, it occurs near the pressure threshold shown in (a).

distributions, because the number occupation statistics are not independent and uncorrelated.

The two-step transport process describes a linear $q-\Delta P$ relationship with nonzero intercept. At equilibrium, however, any system has both zero current and zero pressure drop, so any valid $q-\Delta P$ relationship must go through the origin. The $q-\Delta P$ relationship must therefore have two segments, one linear with nonzero intercept, and a flat segment that connects the origin to the pressure intercept (Figure 3a). The two segments of the $q-\Delta P$ relationship correspond to the two steps in the passage process and the two possible reference states for linear response theory: the wet state and the dry state.

The linear response permeability with respect to the wet state is computed in an equilibrium system at a pressure above the wetting pressure (Figure 4b). For very hydrophobic pores, like those we study here, the equilibrium state at ambient pressure is the dry state, so the linear response permeability with respect to the dry state is computed using equilibrium systems at ambient pressure. When computed in the wet reference state, permeabilities evaluated in linear response roughly match the nonequilibrium wet permeabilities shown in Figure 3b. The linear response permeabilities average poorly, which is the reason for studying them with nonequilibrium techniques.¹²

For a hypothetical macroscopic pore with a true thermodynamic dewetting transition, the linear response permeability computed with respect to the dry state would be vanishingly small, because the probability for fluctuations that allow water to cross the dry pore tend toward zero in the thermodynamic limit. In this limit, the first segment of the $q-\Delta P$ relationship has a slope near zero, as illustrated in Figure 3a. Our system, however, does not have a sharp thermodynamic dewetting transition. In the dry state, there are always fluctuations that wet the pore; there is almost a 30% chance of finding a molecule in the pore (Figure 4b). Some form of the nonlinear description shown in Figure 1 with a non-negligible initial slope is therefore always strictly correct. It remains to be shown that the large system limit and the corresponding simple linear $q-\Delta P$ relationship in Figure 3a is in fact valid for these systems.

In these atomically thin membranes, with pores that admit only single-file water, one might suspect that the large system limit (Figure 3a) of the general nonlinear relationship (Figure 1) is invalid. Indeed, the average pore occupation is approximately three molecules, a far cry from the thermodynamic limit (Figure 4b). In previous work,¹³ we showed that a simple macroscopic thermodynamic argument captures the dewetting contact angle surprisingly well, but this may not extend to more detailed observables like the wetting pressure. To justify the large system limit, we generalize this thermodynamic argument by allowing for more complex pore geometries.

For the thermodynamic analysis, we assume the pore volume is an hourglass-shaped solid of revolution about the pore axis and symmetric about the plane of the membrane. The grand potentials for the liquid and vapor phases inside the pore $\operatorname{are}^{13,21}$

$$\Omega_{\rm l} = -P_{\rm l}V + \gamma_{\rm sl}A_{\rm side} \tag{3}$$

$$\Omega_{\rm v} = -P_{\rm v}V + \gamma_{\rm sv}A_{\rm side} + 2\gamma_{\rm lv}A_{\rm cap} \tag{4}$$

where $A_{\rm side}$ is the area of the side of the solid of revolution, $A_{\rm cap}$ is the area of one of the caps on the end of the solid, V is the volume of the region (Figure 5a), the γ values are surface tensions, and $P_{\rm l}$ and $P_{\rm v}$ are the pressures of the two phases. The absolute free energies in eqs 3 and 4 depend on quantities like $P_{\rm v}$ that are meaningless in systems like ours, where the "vapor phase" is defined by the absence of approximately three molecules. But at the dewetting transition, only the free energy difference $\Delta\Omega \equiv \Omega_{\rm v} - \Omega_{\rm l}$ is important, and these ill-defined quantities appear in comparison with well-defined ones. At the dewetting transition, we have $\Delta\Omega = 0$, so

$$P_{l}^{*} \approx -\frac{\gamma_{lv}}{V} (A_{side} \cos \theta + 2A_{cap})$$
(5)

where we use Young's equation $\gamma_{vl} \cos \theta = \gamma_{sv} - \gamma_{sl}$, ²² P_l^* is the critical wetting pressure, and we neglect P_v , because the vapor pressure of water is five orders of magnitude smaller than the wetting pressures in Figure 4a.

We compare the nonequilibrium pressure thresholds (Figure 4a) to the thermodynamic wetting pressures predicted by eq 5. In ref 13, the pore was assumed to have a cylindrical volume with the length and radius determined by the pore size and equilibrium water density (Figure 5c). There, these assumptions gave a reasonable qualitative agreement with the



Figure 5. (a) A schematic showing a cylindrical pore volume with the area of the side A_{side} , the area of a cap A_{cap} , the volume V, and the length L. This can be easily generalized to an arbitrary solid of revolution, like the parabolic solid in panel (c). (b) The pressure threshold data from Figure 4a (black). The solid lines are predictions of the thermodynamic argument based on eq 5 and panel (a). The blue line uses the pore geometry from ref 13, which is illustrated in blue in panel (c). The red line uses a parabolic pore geometry (eq 6) fit to the black points. The best fit geometry is shown in red in panel (c), with the equilibrium density of water in the background. The gray blocks in (c) are the edges of the pore in the membrane.

critical contact angle observed in nonequilibrium simulation.¹³ Here, these assumptions reproduce the same qualitative trend in wetting pressure that we observe, but the agreement is unsatisfying (Figure 5b). We now explore more complex pore geometries, which are perhaps more faithful to the true "thermodynamic" surface. Further, instead of estimating the pore size from equilibrium density considerations, we turn the problem around and ask the thermodynamics to predict the shape of the pore. To this end, we fit the pressure threshold data to the thermodynamic prediction to find the best-fit pore size parameters.

We fix the pore geometry to be the parabolic solid of revolution given by revolving

$$y(x) = ax^2 + r \tag{6}$$

about the x-axis. More complex solids require too many parameters, and fits are underdefined by the simple form of the pressure threshold data (Figure 5b). The geometry of the pore defined by this revolved parabola depends on three parameters: its radius at the narrowest point r, its length L, and the curvature of the side wall a. The cylindrical case shown in Figure 5a corresponds to $a = 0 \text{ Å}^{-1}$. We fit these parameters to the pressure threshold data in Figure 5b, treating a negative wetting pressure as a pressure threshold of zero. Since the nonzero data in Figure 5b appear linear, one might worry about fitting three parameters to these data, but with reasonable initial guesses, the fit converges well. Using $\gamma_{lv} = 72.1 \text{ mJ/m}^2$ for water, the best-fit pore geometry has L = 8.0 Å, r = 1.3 Å, and $a^{-1} = 64$ Å, which describes the equilibrium water density in a wetted pore amazingly well (Figure 5c). It is phenomenal that a simple argument based on macroscopic thermodynamics can, in one stroke, capture both the equilibrium density of water inside the pore and the nonequilibrium wetting pressure for flow through the pore.

The surprising success of this macroscopic argument to capture the pressure threshold data suggests that the two-step transport mechanism with a thermodynamically well-defined pressure threshold is indeed a valid concept in this system. If the wetting transition were not sharp, this would not be the case, and we would be forced to understand the system in terms of the more complex nonlinear relationship presented in Figure 1. Instead, we find that the pressure threshold is valid, the transition is sharp, and the $q-\Delta P$ relationship can be described by its slope and pressure intercept alone. While the nonlinear $q-\Delta P$ relationship proposed in Figure 1 is strictly correct, this system is deep in the limit where the initial shallow slope is effectively zero, and the linear description is valid. This provides a simple and intuitive picture of the passage process that is also more accurate than the conventional description.

On single-layer membranes, there is not a sufficient distinction between the wet and dry states to perform a similar analysis. The critical dewetting contact angle is larger on single-layer membranes. As a result, the simulations we explore here and in ref 13 do not take place in a putative dry state. The dry state might be accessible at larger contact angles, or perhaps the existence of such a state is entirely washed out by fluctuations in the smaller single-layer pore volume. In either case, it is remarkable that this thermodynamic model captures the behavior of the double-layer membranes.

In very hydrophobic atomically thin porous membranes, the pores are dry at ambient pressure. Water transport in these membranes becomes a two-step process, where the externally applied pressure ΔP induces wetting, and transport occurs from the wet state. The water current is near zero until $\Delta P > \Delta P_{\rm T}$. This two-step behavior is a simple nonlinearity with respect to the dry state at standard temperature and pressure. In the wet state, the system obeys linear response.

A similar explanation of, and resolution to, an apparently nonlinear phenomena has been proposed for aqueous solvation dynamics.¹⁹ Our model may also explain the nonlinearities observed in the current–voltage relationships for ions passing through nanopores,²³ although that study used much larger nanopores and focused on the ion current, not the water current.

In the system we study, even with only three molecules in the pore, the pore is close enough to the macroscopic limit that the transition to the wet state is sharp and linear response theory about the wet state fully describes the transport process. This simple thermodynamic argument captures both the equilibrium density of water inside a pore and the wetting pressure for the dry pores.

From a naive perspective, a very hydrophobic pore has a high permeability. But in actual applications for RO, one can only achieve this permeability after applying a pressure drop on the order of 0.5 GPa. Such backing pressures are not only prohibitively large for RO facilities, but they are likely to mechanically destroy the membranes.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Joel.Eaves@colorado.edu.

ORCID ⁰

Steven E. Strong: 0000-0003-4204-3028 Joel D. Eaves: 0000-0002-9371-1703

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank R. Rapf for input about the origin of life literature, and we thank V. Vaida for many interesting scientific discussions over the years. This work utilized the Janus supercomputer, which is supported by the National Science Foundation (Grant No. CNS-0821794) and the Univ. of Colorado Boulder. The Janus supercomputer is a joint effort of the Univ. of Colorado Boulder, the Univ. of Colorado Denver, and the National Center for Atmospheric Research. This material is based upon work supported by the National Science Foundation under Grant No. CHE-1455365 and a Graduate Research Fellowship under Grant No. DGE-1144083.

REFERENCES

(1) Dobson, C. M.; Ellison, G. B.; Tuck, A. F.; Vaida, V. Atmospheric Aerosols as Prebiotic Chemical Reactors. *Proc. Natl. Acad. Sci. U. S. A.* **2000**, *97*, 11864–11868.

(2) Szostak, J. W.; Bartel, D. P.; Luisi, P. L. Synthesizing Life. *Nature* 2001, 409, 387–390.

(3) Zhu, T. F.; Szostak, J. W. Coupled Growth and Division of Model Protocell Membranes. J. Am. Chem. Soc. 2009, 131, 5705–5713.

(4) Cape, J. L.; Monnard, P.-A.; Boncella, J. M. Prebiotically Relevant Mixed Fatty Acid Vesicles Support Anionic Solute Encapsulation and Photochemically Catalyzed Trans-Membrane Charge Transport. *Chem. Sci.* **2011**, *2*, 661–671.

(5) Maurer, S. E.; Monnard, P.-A. Primitive Membrane Formation, Characteristics and Roles in the Emergent Properties of a Protocell. *Entropy* **2011**, *13*, 466–484.

(6) Black, R. A.; Blosser, M. C.; Stottrup, B. L.; Tavakley, R.; Deamer, D. W.; Keller, S. L. Nucleobases Bind to and Stabilize Aggregates of a Prebiotic Amphiphile, Providing a Viable Mechanism for the Emergence of Protocells. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 13272–13276.

(7) Saha, R.; Pohorille, A.; Chen, I. A. Molecular Crowding and Early Evolution. *Origins Life Evol. Biospheres* **2014**, *44*, 319–324.

(8) Suk, M. E.; Aluru, N. R. Water Transport Through Ultrathin Graphene. J. Phys. Chem. Lett. 2010, 1, 1590–1594.

(9) Cohen-Tanugi, D.; Grossman, J. C. Water Desalination Across Nanoporous Graphene. *Nano Lett.* **2012**, *12*, 3602–3608. (10) Cohen-Tanugi, D.; Grossman, J. C. Water permeability of Nanoporous Graphene at Realistic Pressures for Reverse Osmosis Desalination. J. Chem. Phys. **2014**, 141, 074704.

(11) Surwade, S. P.; Smirnov, S. N.; Vlassiouk, I. V.; Unocic, R. R.; Veith, G. M.; Dai, S.; Mahurin, S. M. Water Desalination Using Nanoporous Single-Layer Graphene. *Nat. Nanotechnol.* **2015**, *10*, 459–464.

(12) Strong, S. E.; Eaves, J. D. Atomistic Hydrodynamics and the Dynamical Hydrophobic Effect in Porous Graphene. *J. Phys. Chem. Lett.* **2016**, *7*, 1907–1912.

(13) Strong, S. E.; Eaves, J. D. The Dynamics of Water in Porous Two-Dimensional Crystals. J. Phys. Chem. B 2017, 121, 189–207.

(14) Ostrowski, J. H. J.; Eaves, J. D. The Tunable Hydrophobic Effect on Electrically Doped Graphene. *J. Phys. Chem. B* **2014**, *118*, 530–536. (15) Werder, T.; Walther, J. H.; Jaffe, R. L.; Halicioglu, T.; Koumoutsakos, P. On the Water-Carbon Interaction for Use in

Molecular Dynamics Simulations of Graphite and Carbon Nanotubes. J. Phys. Chem. B 2003, 107, 1345–1352.

(16) Frenkel, D.; Smit, B. Understanding Molecular Simulation: From Algorithms to Applications, 2nd ed.; Academic Press: San Diego, CA, 2001.

(17) Zwanzig, R. Nonequilibrium Statistical Mechanics; Oxford University Press: Oxford, England, 2001.

(18) Kittel, C. Introduction to Solid State Physics, 2nd ed.; Wiley: New York, 1963.

(19) Geissler, P. L.; Chandler, D. Importance Sampling and Theory of Nonequilibrium Solvation Dynamics in Water. *J. Chem. Phys.* 2000, *113*, 9759–9765.

(20) Zhu, F.; Tajkhorshid, E.; Schulten, K. Collective Diffusion Model for Water Permeation through Microscopic Channels. *Phys. Rev. Lett.* **2004**, *93*, 224501.

(21) Huang, X.; Margulis, C. J.; Berne, B. J. Dewetting-Induced Collapse of Hydrophobic Particles. *Proc. Natl. Acad. Sci. U. S. A.* 2003, 100, 11953–11958.

(22) Young, T. An Essay on the Cohesion of Fluids. *Philos. Trans. R. Soc. London* 1805, 95, 65–87.

(23) Powell, M. R.; Cleary, L.; Davenport, M.; Shea, K. J.; Siwy, Z. S. Electric-Field-Induced Wetting and Dewetting in Single Hydrophobic Nanopores. *Nat. Nanotechnol.* **2011**, *6*, 798–802.