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The Dynamics of Water in Porous Two-Dimensional Crystals

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ABSTRACT: Porous two-dimensional crystals offer many promises for water desalination applications. For computer simulation to play a predictive role in this area, however, one needs to have reliable methods for simulating an atomistic system with hydrodynamic currents and interpretative tools to relate microscopic interactions to emergent macroscopic dynamical quantities, such as friction, slip length, and permeability. In this article, we use Gaussian dynamics, a nonequilibrium molecular dynamics method that provides microscopic insights into the interactions that control the flows of both simple liquids and liquid water through atomically small channels. In simulations of aqueous transport, we mimic the effect of changing the membrane chemical



composition by adjusting the attractive strength of the van der Waals interactions between the membrane atoms and water. We find that the wetting contact angle, a common measure of a membrane's hydrophobicity, does not predict the permeability of a membrane. Instead, the hydrophobic effect is subtle, with both static and dynamic effects that can both help and hinder water transport through these materials. The competition between the static and dynamical hydrophobicity balances an atomic membrane's tendency to wet against hydrodynamic friction, and determines an optimal contact angle for water passage through nonpolar membranes. To a reasonable approximation, the optimal contact angle depends only on the aspect ratio of the pore. We also find that water molecules pass through the most hydrophobic membranes in a punctuated series of bursts that are separated by long pauses. A continuous-time Markov model of these data provides evidence of a molecular analogue to the clogging transition, a phenomenon observed in driven granular flows.

1. INTRODUCTION

The hydrophobic effect is one of the most important and elementary phenomena in chemistry.¹⁻¹⁷ On macroscopic scales, it is the driving force that partitions oily and aqueous solutions, and on molecular length scales, it shapes the folding pathways of proteins and reinforces the stability of biomolecules.^{1,18} Advancing the qualitative and conceptual underpinnings of the hydrophobic effect into quantitative theory remains a grand challenge in physical chemistry. The majority of work in this field has focused on solvation and aqueous chemistry, where the hydrophobic effect is thermodynamic in nature and depends solely on the statistical mechanics of intermolecular configurations.^{15–27} In these aspects of chemistry, hydrophobicity derives from molecular statics. The simplest example comes from the wetting of solid surfaces, where one measures the surface's hydrophobicity through the contact angle.²⁸⁻³⁰ For a droplet resting on a surface, the contact angle is a function of the liquid-solid surface tension.^{31,32} But, in dynamical contexts, quantifying the hydrophobic effect is more complicated. For a rolling droplet, the contact angle depends on other dynamical quantities and the surface tension becomes an incomplete predictor of wetting.^{30,33-35}

In this article, we bring new attention to the dynamical roles that the hydrophobic effect plays in aqueous transport. Motivated by applications to water desalination, we study aqueous flow through porous two-dimensional (2d) crystals using graphene as a model system. $^{36-39}$ In water desalination, the size of the hydrated ion to be blocked dictates the size of the pore, so the throughput is bottlenecked by how fast one can push water across the membrane. One figure of merit that quantifies the throughput for a semipermeable membrane is the permeability, which is proportional to the slope of the mass flux versus the applied pressure.^{40,41} Although the hydrodynamics appropriate for water desalination is at low Reynolds number (Re) and transport takes place close to thermal equilibrium, computing the permeability from simulations at thermal equilibrium is computationally impractical.^{40,42} To address this problem, we have developed Gaussian dynamics (GD), which is an atomistic simulation method that allows one to simulate a fluid away from thermodynamic equilibrium and under flow, and is also faithful to statistical mechanics and hydrodynamics.⁴⁰ In Section 2, we present a thorough derivation and discussion of GD. Hydrodynamic currents emerge naturally in simulations using GD, and from them one can compute hydrodynamic-like transport properties by systematic averaging without imposing a priori knowledge of boundary conditions or flow profiles.

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In previous work,⁴⁰ we compared GD with a fixed gradient protocol for nonequilibrium molecular dynamics, the "pump method",⁴³ and with predictions from linear response theory.⁴ In Section 3.1, we discuss the similarities and differences between GD and the pump method in more detail for both Poiseuille flow and flow through porous walls. These two methods do not always give the same results for the permeability, and the deviations between the two are rooted in the fluctuations that each method allows. Because GD admits density and pressure fluctuations, it permits flow through pores in superhydrophobic membranes where the pump method does not. In Section 3.2, we present a thorough discussion of the calculation of the pressure profile and pressure drop, which are used to compute the permeability. In Section 3.3, we use simple liquids as model systems to investigate the hydrodynamic slip length, which measures the deviation from the idealized "noslip" boundary condition.44 The slip length in simulations of water in carbon nanotubes has been a topic of controversy, with different simulation methods yielding different results.^{45–51} Our results show that the slip length depends sensitively on how one holds the membrane atoms in place, either through a rigid constraint or with harmonic springs. The slip length depends much less sensitively on whether the membrane atoms or the fluid atoms are thermostatted. These observations have not been discussed in the literature and may be at least partly responsible for some apparent disagreement between different studies.

While graphene has been the workhorse system for water desalination applications, it is now feasible to produce highquality samples of other 2d crystals, such as MoS₂ and BN.⁵² It is possible that these materials could outperform graphene and it is therefore imperative to understand the types of intermolecular interactions that lead to fast water transport through these emerging membranes. Rather than studying specific candidate 2d crystals, we cast a broader net and tune the intermolecular potentials between the water molecules and the membrane parametrically so that we can answer general questions about what governs water transport through these materials. We refer to these atomically thin model membranes as "atomic membranes." The results of this study appear in Section 3.4. In our models, the intermolecular interactions come in two flavors, polar interactions and van der Waals interactions. These two classes of interactions between water and membrane atoms can both tune the wetting contact angle, but the dynamics of water passage depends sensitively on which class is dominant. Two membranes having different interaction types but with the same contact angles, pore geometries, and pore sizes will not necessarily have the same permeabilities. Furthermore, the fluid flow endows the hydrophobic effect with both static and dynamic parts. The static contribution of the hydrophobic effect manifests as a tendency for the liquid to wet the pore and can be understood in terms of equilibrium thermodynamics.^{17,24,57} The dynamical aspects of hydrophobicity emerge as resistance, or friction, between the liquid and the solid surface. Indeed, the competition between the static and dynamic hydrophobicity determines the optimal permeability for a given membrane.

Finally, in Section 3.5, we find regimes where water transport deviates from a simple biased Markov random walk model, which is fundamental to the linear response theories that describe water transport near equilibrium.⁴¹ We find that sharp bursts and long pauses dominate the mass current through the pores in the most hydrophobic membranes, and we analyze

these dynamics using a continuous-time random walk (CTRW) model. The waiting-time distribution shows the onset of a power-law decay and the burst-size distribution is an exponential. These two features are signatures of the clogging transition observed in granular systems.^{58–62} Interestingly, in this parameter space, the clogging phenomenon is a unique feature of the hydrogen bonding dynamics of water and cannot be explained purely by the granular nature of water on a molecular scale.

2. METHODS

2.1. Derivation of GD. GD is rooted in Gauss's principle of least constraint, which finds the equations of motion that strictly obey a set of constraints but that generate dynamics as mathematically close as possible to unconstrained Newtonian mechanics.^{63,64} This is similar in spirit to other constraint methods, such as Euler–Lagrange constraint dynamics and extended Lagrangian ensembles, that have a long history in molecular dynamics simulations.⁶⁵ We start by first discussing the constraints and then discuss Gauss's method to satisfy them. It is trivial to constrain the positions of atoms that are fixed in space, so we do not include them in this discussion. For a system of N atoms with masses $\{m\}$ at positions $\{\mathbf{r}\}$, the constraint that holds the total mass flux constant, written as a level set \mathbf{g}_{f} , is

$$\mathbf{g}_{\mathrm{f}}(\{\dot{\mathbf{r}}\}) = \frac{1}{M} \sum_{i=1}^{N} m_{i} \dot{\mathbf{r}}_{i} - \mathbf{u}_{\mathrm{COM}} = 0$$
(1)

where $M \equiv \sum_{i=1}^{N} m_i$ is the total mass of the system, overdots denote time derivatives, and \mathbf{u}_{COM} is the center-of-mass (COM) velocity of the fluid which is held constant. For compactness of notation, we suppress time dependence. Although out of equilibrium, the flows that we study are at steady state. To satisfy the constraint in eq 1, an external force will drive the system and heat it. A thermostat must dissipate this heat to maintain steady state, which requires another constraint.

To develop a thermostat, one needs a working definition of temperature. Following previous work,⁶³ we assume that the velocity of an atom in the lab frame $\dot{\mathbf{r}}_i$ can be decomposed into a thermal part \mathbf{v}_i and a streaming part $\mathbf{u}(\mathbf{r}_i)$,

$$\dot{\mathbf{r}}_i = \mathbf{v}_i + \mathbf{u}(\mathbf{r}_i) \tag{2}$$

which implies that the flows are not turbulent. With this decomposition, we assume local equilibrium and define the kinetic temperature with respect to the thermal, or peculiar, velocities $\mathbf{v}_i^{.63,66}$ The thermal velocities have zero mean and a standard deviation given by equipartition. The streaming velocities

$$\mathbf{u}(\mathbf{r}) = \frac{\sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i \delta(\mathbf{r}_i - \mathbf{r})}{\sum_{i=1}^{N} m_i \delta(\mathbf{r}_i - \mathbf{r})}$$
(3)

must be determined self-consistently, which we achieve by spatial averaging. Figure 1 depicts the resolution of the Dirac δ -functions in eq 3 by spatial binning. These considerations lead to the following temperature constraint

$$g_{\rm T}(\{\mathbf{r}, \, \dot{\mathbf{r}}\}) = \frac{1}{2} \sum_{i=1}^{N} m_i (\dot{\mathbf{r}}_i - \mathbf{u}(\mathbf{r}_i))^2 - \frac{d(N - N_u)k_{\rm B}T}{2} = 0$$
(4)



Figure 1. Image of a 2d Lennard-Jones (LJ) simulation illustrating the calculation of the streaming velocity profile, $\mathbf{u}(\mathbf{r})$. The blue points are the fluid atoms and the gray points are the wall atoms. The gray boxes, fixed in the lab frame, represent the resolution for $\mathbf{u}(\mathbf{r})$, with a linear dimension typically on the order of a few atomic diameters. The streaming velocity within each bin is the COM velocity of the atoms in that cell.

where $k_{\rm B}$ is Boltzmann's constant, T is the temperature setpoint, d is the dimensionality, and $N_{\rm u}$ is the number of bins used to compute the streaming velocity profile (Figure 1). At equilibrium, this constraint (eq 4) generates the well-known Gaussian isokinetic thermostat.^{63,64,67,68} Because the form of the velocity profile is not assumed a priori but is determined self-consistently a posteriori, the constraint in eq 4 leads to a profile-unbiased thermostat (Figure 1).⁶⁹ Equation 4 pertains to the situation where only the fluid atoms are thermostatted. In general, the thermostatted atoms may or may not be the same as the fluid atoms constrained in eq 1. For example, when a system consists of a fluid flowing between walls, if the wall atoms are mobile, then either the fluid, the walls, or both can be thermostatted. If both the fluid and the walls are thermostatted, then the thermostat constraint will couple the momenta of fluid atoms to the momenta of wall atoms, rendering the COM momentum of the fluid unconserved. Instead, both the wall and fluid atoms can be thermostatted simultaneously with a separate thermostat for each.

The constraints in eqs 1 and 4 depend on the velocities, making them nonholonomic constraints.⁷⁰ It is difficult to satisfy nonholonomic constraints using Euler–Lagrange constraint dynamics,^{71,72} so we turn instead to Gauss's principle of least constraint, which finds the accelerations that minimize the cost function

$$C(\{\mathbf{r}, \, \dot{\mathbf{r}}, \, \ddot{\mathbf{r}}\}) = \frac{1}{2} \sum_{i=1}^{N} m_i \left(\ddot{\mathbf{r}}_i - \frac{\mathbf{F}_i}{m_i}\right)^2 + \lambda_{\mathrm{T}} \dot{\mathbf{g}}_{\mathrm{T}} + \lambda_{\mathrm{f}} \cdot \dot{\mathbf{g}}_{\mathrm{f}}$$
(5)

where $\mathbf{F}_i = -\nabla_i U$ is the force on atom *i* from the intermolecular potential *U*, and the λ s are Gaussian multipliers. In the absence of the constraints, the accelerations that minimize eq 5 follow Newton's law $m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i$. The constraints given in eqs 1 and 4 do not depend on the accelerations, so to minimize eq 5 with respect to the accelerations, we write the constraints as functions of the accelerations by differentiating them with respect to time.⁶³ Including geometry constraints, such as rigid bonds, is trivial because those constraints are holonomic; they depend only on positions and separate completely. Here, we ignore the temperature constraint to illustrate the solution process. For the full treatment, see the Supporting Information in ref 40. The time derivative of eq 1 is

$$\dot{\mathbf{g}}_{f} = \sum_{i=1}^{N} m_{i} \ddot{\mathbf{r}}_{i} = 0 \tag{6}$$

which gives the cost function

$$C(\{\ddot{\mathbf{r}}\}) = \frac{1}{2} \sum_{i=1}^{N} m_i \left(\ddot{\mathbf{r}}_i - \frac{\mathbf{F}_i}{m_i}\right)^2 + \lambda_f \cdot \sum_{i=1}^{N} m_i \ddot{\mathbf{r}}_i$$
(7)

We now find the accelerations that minimize the cost function

$$\frac{\partial}{\partial \ddot{\mathbf{r}}_{i}} C(\{\ddot{\mathbf{r}}\}) = m_{i} \left(\ddot{\mathbf{r}}_{i} - \frac{\mathbf{F}_{i}}{m_{i}} \right) + \lambda_{f} m_{i} = 0$$
(8)

This gives the equation of motion

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i - \lambda_f m_i \tag{9}$$

We solve for λ_f by summing eq 9 over all the atoms

$$\sum_{i=1}^{N} m_i \ddot{\mathbf{r}}_i = \sum_{i=1}^{N} \mathbf{F}_i - \lambda_f \sum_{i=1}^{N} m_i$$
(10)

The term on the left-hand side is zero due to eq 6, so we find

$$\lambda_{\rm f} = \frac{1}{M} \sum_{i=1}^{N} \mathbf{F}_i \tag{11}$$

The resulting equation of motion is

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i - m_i \mathbf{I} \tag{12}$$

where we have defined the vector

$$\mathbf{I} \equiv \boldsymbol{\lambda}_{\rm f} = \frac{1}{M} \sum_{i=1}^{N} \mathbf{F}_{i}$$
(13)

I is an acceleration, not the identity matrix.

Including the Gaussian isokinetic thermostat and molecular geometry constraints would simply add more terms to the equation of motion 40

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i - m_i \mathbf{I} - m_i \xi (\dot{\mathbf{r}} - \mathbf{u}(\mathbf{r}_i)) + \mathbf{f}_i$$
(14)

where, for molecules, \mathbf{f}_i is the force of constraint that fixes the intramolecular geometry,^{73,74} and ξ is the drag coefficient associated with a profile-unbiased Gaussian isokinetic thermostat^{63,64,67–69}

$$\xi \equiv \frac{\sum_{i=1}^{N} (\dot{\mathbf{r}}_{i} - \mathbf{u}(\mathbf{r}_{i})) \cdot \mathbf{F}_{i}}{\sum_{i=1}^{N} m_{i} (\dot{\mathbf{r}}_{i} - \mathbf{u}(\mathbf{r}_{i}))^{2}}$$
(15)

Instead of exactly satisfying the temperature constraint at each time step, we fix the average kinetic temperature using a profileunbiased Nosé–Hoover thermostat.^{63,69,75,76} This greatly improves computational speed. Note that the final equation of motion (eq 14) does not depend on the COM momentum set point \mathbf{u}_{COM} . This means that GD only preserves the initial COM momentum. As such, one must initialize the system with a nonzero COM momentum to simulate a steady-state flow. Section 2.4 discusses this and the equilibration to steady state in detail.

The flow constraint applies a driving force to each fluid atom equal to $-m_i$ I. Physically, I is a gravitational field that fluctuates in time to maintain the mass flux through the system. In practical applications, I is weak. In 2d LJ simulations, even at *Re* around 10, the average applied force is approximately equal to the force between two LJ atoms separated by 3 σ . This force is so weak that it is beyond the cutoff distance typically employed in simulations.



Figure 2. Snapshot from a 2d simulation using the pump method, with the pump region outlined in orange. An external force, applied only to the atoms in the pump region, creates a pressure drop across the pore, situated in the middle of the image. The simulation box must be long enough so that the bulk fluid can equilibrate the pressure and spatially discontinuous force applied in the pump region. In our simulations, the pump region is 5 σ wide and is centered on the periodic boundary. For clarity, the pump region shown here is shifted and not drawn to scale.

Equation 12 was first derived in ref 40 and is the basis of the GD method. It is simple, but it is theoretically rigorous, unlike many common nonequilibrium methods that employ ad hoc combinations of external forces, particle swaps, and thermostats.^{43,44,77–82} GD is computationally inexpensive because computing I scales as O(N). GD also consistently averages more quickly than both the pump method and linear response theory.⁴⁰

2.2. 2d LJ Simulations. To understand some of the differences between GD and another common method for the simulation of steady-state flow, we perform some comparisons using a 2d LJ test system. We compare GD to the "pump method", in which a force is applied only to atoms in a "pump region", which is a region far from the region of interest, such as a pore (Figure 2).⁴³ In some applications of the pump method, the force per atom is constant in time. In our implementation, the total force on the pump region is constant in time, which results in a constant pressure drop ΔP across the system. Provided the pump region is large enough that the particle number fluctuations in its volume are small, the differences between these two implementations are negligible. In many respects, the pump method is a constant gradient complement to GD, which is a constant current method.

We study flows in two different geometries, Poiseuille flow and flow through a porous wall. The simulation geometry for flow through a porous wall is illustrated in Figures 2 and 5b. The simulations are periodic in both dimensions. Poiseuille flow is flow between two parallel infinite walls (Figure 5a), and the simulations are only periodic in the direction of flow. The wall and fluid atoms are identical. We make the wall–fluid interaction purely repulsive by cutting the force off where it goes to zero, at $2^{1/6}\sigma$.⁸³ The wall atoms are fixed in space during the simulations.

2.3. Water Simulations. We model water using the rigid SPC/E potential.^{84,85} The atomic membranes have the same geometries as single- and double-layer graphene, and the membrane atoms remain fixed in space during the simulations. The pores in the membranes are designed to admit single-file water (Figure 3). We allow the membrane and oxygen atoms to interact through van der Waals forces, which we model with a LJ potential, $U(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]$. Using graphene as a reference system, we tune the van der Waals part of the hydrophobicity by changing the ϵ parameter for the carbonoxygen LJ interaction, while keeping σ fixed. Over the range of ϵ values we study, Werder et al. found that the contact angle of a water drop on a double-layer 2d crystal varies linearly from about 30° to 140° in simulations.⁸⁶ By changing ϵ and not σ , we aim to tune the hydrophobicity with the pore size fixed. In a statistical definition of the pore size based on, for example, the theory of Weeks, Chandler, and Andersen for a homogeneous fluid,⁸³ the effective hard-sphere diameter of the membrane atoms would vary with ϵ , so the pore size would also depend on ϵ . Because there are only a few water molecules in the pore and



Figure 3. The single-layer membrane pore (a, b) and the double-layer membrane pore (c, d). The light gray atoms depict the bottom layer of the double-layer membrane. Nearly identical in shape, both pores have the same atom-to-atom distance (7.4 Å). The pores are only wide enough to allow single-file water transport (b, d). We use the density of water in the vicinity of the pore (e) to define the length of the pore L (eq 28), and the region indicated by a red box is used to calculate n(t) (Section 2.4). This region has a length L along the x axis. The density scale is above, with red lines indicating the edges of the boxed region.

the environment there is anisotropic, we expect a mechanical criterion for the pore size to be more accurate. Mechanically, the pairwise membrane—water force goes to zero at $2^{1/6}\sigma$, and is independent of ϵ . Regardless, if one were to employ the statistical criterion for the pore size, over the full range of ϵ explored here, the channel diameter only changes by about 5%.

2.4. Steady State and Current. Just as equilibrium simulations require equilibration time to "forget" their initial conditions, both GD and the pump method require "stabilization" time to reach steady state. Furthermore, GD only maintains the COM momentum that is already present in a system. As such, a nonequilibrium simulation must be initialized by giving the system a total COM momentum. We do this by first equilibrating the system at thermal equilibrium and then adding a velocity in the direction of flow to all fluid atoms. During the stabilization time, this uniform velocity profile relaxes into the natural steady-state velocity profile. The flux profile

$$\mathbf{J}(\mathbf{r}, t) = \rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t)$$
(16)

measures whether or not the system has achieved steady state, where

$$\rho(\mathbf{r}, t) = \sum_{i} m_{i} \delta(\mathbf{r}_{i}(t) - \mathbf{r})$$
(17)

is the mass density field.

Mass conservation implies the continuity equation

$$\nabla \cdot \mathbf{J}(\mathbf{r}, t) = -\frac{\partial \rho(\mathbf{r}, t)}{\partial t}$$
(18)

which requires that the flux profile is constant in both space and time when the system is at steady state, $\partial_t \rho = 0 \Rightarrow \nabla \cdot \mathbf{J}(\mathbf{r}) = 0$. In the 2d LJ simulations, we use this criterion directly to ensure that the system is at steady state (Figure 5c,d). In the water simulations, however, the low flow rates make the flux profiles too noisy to give a good test of steady state, so we use a coarser criterion on the flux. We compare the current inside the pore with the global current q, defined below, to test that the flux profile is constant in space. A simulation is at steady state when the current inside the pore is equal to the global current, within the noise.

The computation of the global current requires that we develop relationships between the total mass flux J_{tot} , the COM velocity \mathbf{u}_{COM} , and the global particle current, q, at steady state. The total mass flux J_{tot} is defined as a spatial average of the flux profile $\mathbf{J}(\mathbf{r}, t)$ over the entire simulation box

$$\mathbf{J}_{\text{tot}} \equiv \frac{\int_{\text{box}} d^d \mathbf{r} \, \mathbf{J}(\mathbf{r}, t)}{\int_{\text{box}} d^d \mathbf{r}}$$
(19)

where $\int_{box} d^d r$ denotes an integral over a *d*-dimensional simulation box. The denominator in eq 19 is simply the *d*-dimensional volume of the simulation, including any volume excluded by obstacles. Inserting eqs 3 and 17 into eq 16 and performing the integration in eq 19 yields

$$\mathbf{J}_{\text{tot}} = \rho_{\text{tot}} \mathbf{u}_{\text{COM}} \tag{20}$$

where $\boldsymbol{u}_{\text{COM}}$ is the COM velocity of the fluid and in three dimensions

$$\rho_{\rm tot} = \frac{M}{L_x L_y L_z} \tag{21}$$

is the *total* mass density in the simulation, and L_x , L_y , and L_z are the simulation box dimensions along the appropriate axes. $\rho_{\rm tot}$ is *not* the same as the bulk fluid density ρ_0 , which is the average fluid density in the homogeneous part of the fluid far from the membrane.

In what follows, for clarity, we specify our discussion to three dimensions, though the derivation in two dimensions appropriate for the LJ simulations reported here is straightforward. In our simulations, only the *x*-component of \mathbf{u}_{COM} is nonzero on average, so eq 20 simplifies to $J_{\text{tot},x} = \rho_{\text{tot}} u_{\text{COM},x}$. The global particle current through a system with cross-sectional area *A* normal to the current is

$$q = \frac{J_{\text{tot},x}A}{m_{\text{p}}} \tag{22}$$

where m_p is the mass per particle. For a three-dimensional box with flow along the *x* axis, $A = L_y L_z$, and eqs 20–22 yield the desired relationship between the global particle current *q* and $u_{\text{COM},x}$

$$u_{\text{COM},x} = \frac{qL_x}{N} \tag{23}$$

To simulate a given current, one uses eq 23 to find the initial set-point velocity $u_{COM,x}$ for the simulation. Choosing an appropriate value of q is a balancing act. If q is too large, the equilibration time to steady state becomes too long, and the requisite value of L_x becomes too large to be computationally feasible. If q is too small, more simulations are required to achieve statistically significant data. The particulars depend on the specific system, but for the water simulations reported here, q is on the order of 10 molecules/ns. A more detailed discussion appears in Section 2.6.

We now turn to the calculation of the current inside the pore, which at steady state must be equal to the global current. To compute the current through the pore, we use the collective variable n(t) defined by Zhu et al. in the context of collective diffusion.⁴¹ n(t) is the appropriate collective variable for linear response theory for water flowing through atomic membranes.^{40,41} The variable n(t) is simply a continuous variable that counts net passage events and is defined by integrating

$$dn = \sum_{i}^{\text{in pore}} \frac{dx_i}{L}$$
(24)

forward in time with n(0) = 0, where the sum is over molecules inside some region defined as the "pore", and *L* is the length of the pore region (Figures 2 and 3e). A molecule that moves forward across the pore has dx = L and will increment *n* by exactly 1. A molecule that moves backward across the pore will have dx = -L and will increment *n* by exactly -1. The current is therefore given by the slope of n(t), which we compute by linear regression with zero intercept. The choice of the pore region is discussed in Section 2.6.

2.5. Permeability. For a semipermeable membrane, the "osmotic permeability" quantifies the ease with which a solvent passes through a porous membrane.⁴¹ The osmotic permeability p is the transport coefficient that relates a concentration difference to the osmotic current that it generates

$$q_n = p\Delta C \tag{25}$$

where ΔC is the difference in solute concentration in moles per liter across a membrane that gives rise to a current of solvent $q_n = q/N_A$ in mol/s.⁴¹ In a simulation, it is much easier to drive a current with GD than with a concentration gradient, but to calculate *p*, we must make contact with eq 25. Because we can compute the pressure drop in a simulation (Section 3.2), we replace the concentration difference in eq 25 with the equivalent osmotic pressure that it would generate. For an ideal solution, the van't Hoff equation gives the osmotic pressure

$$\Delta P = N_{\rm A} k_{\rm B} T \Delta C \tag{26}$$

Equations 25 and 26 yield our definition of the permeability⁴⁰

$$p = k_{\rm B} T \frac{q}{\Delta P} \tag{27}$$

which expresses the relationship between the current q and the pressure drop ΔP . GD specifies the current and computes the pressure drop,⁴⁰ whereas the pump method specifies the pressure drop and computes the current.⁴³ A detailed discussion of the calculation of ΔP appears in Section 3.2.

Because atomic membranes are so promising for nextgeneration reverse osmosis (RO), we also report the *approximate* "improvement factor" p/p_0 over the permeability of conventional RO membranes p_0 . We use $p_0 \approx 0.02$ liters of water filtered per cm² of membrane per applied MPa per day,⁵² and assume a membrane porosity of 10% by area³⁷ and a circular pore with diameter 7.4 Å. Note that, in our simulations, the membrane is 3.9% porous by area.

2.6. Simulation Details. The 2d LJ simulations are composed of three parts, 10 τ of equilibration time, 1000 τ of stabilization time, and 1000 τ of data collection, with $\tau \equiv \sqrt{m\sigma^2/\epsilon}$. The time step is 0.001 τ . All of the simulations are at constant number, volume, and temperature (NVT). We use a Nosé–Hoover thermostat with a 0.1 τ damping time.^{75,76} The thermostat is profile-unbiased and uses boxes that contain an average of eight atoms (Figure 1).⁶⁹ We choose the size of the boxes to be large enough so that the COM velocity in a box is not dominated by individual atoms entering or leaving the box, but small enough so that a realistic flow profile can develop. The bulk density of fluid atoms is $\rho_0 = 0.8 \sigma^{-2}$, the temperature is $T = 2 \varepsilon / k_{\rm B}$, and the flow is in the x direction. The wall atoms are separated by 1 σ . For Poiseuille flow, the simulation box is 200 \times 60 σ^2 except for the slip length simulations (Section 3.3), where it is 200 \times 30 σ^2 . For the porous wall flow simulations, the simulation box is $400 \times 60 \sigma^2$.

The water simulations start with 200 ps of bulk water equilibration at 1 atm and 298 K, at constant number, pressure, and temperature (NPT). We then add the atomic membrane and remove any water molecules that overlap it. We equilibrate the system again at NPT for 200 ps, only allowing for expansion/contraction in the x direction because the atomic membrane in the yz plane should not be deformed. After both of the NPT steps above, the box is linearly scaled over 100 ps to its average size during the NPT run. We then add an initial COM momentum in the *x* direction, turn on GD, and stabilize the system for at least 2 ns. The simulations of more hydrophobic membranes require 4, 7, or 9 ns of stabilization time. We then collect data for 5 ns. The simulation time step is 2 fs. The thermostat is a profile-unbiased Nosé-Hoover thermostat with a 200 fs damping time and boxes that contain an average of four molecules (Figure 1). The simulation box is about $62 \times 37 \times 30$ Å³ with 2060 water molecules for singlelayer membranes, and $68 \times 37 \times 30$ Å³ with 2190 water

molecules for double-layer membranes. The exact value of L_x and the number of water molecules vary because of the NPT equilibration and removal of water molecules when the membrane is added. The simulations are periodic in all dimensions. We use the particle–particle particle–mesh method to compute long-range Coulombic forces.⁸⁷

The calculations of the current through the pore (Section 2.4) and the pressure drop (Section 3.2) both require the definition of the length of the pore *L* or a "pore region", where *L* is the length of the pore region in the direction of flow (Figures 2 and 3e). In both the LJ and water simulations, the pore region is symmetric about the plane x = 0. In the LJ simulations, the edges of the pore are defined by the length of the pore $x_{edge} = \pm L/2$. The length of the pore is defined as $L = L_c + 2^{7/6} \sigma$, where L_c is the center-to-center distance of wall atoms at the ends of the pore, and σ is the LJ parameter for wall-fluid interactions. In the water simulations, the edge of the pore x_{edge} is defined as the place where the equilibrium density profile $\rho(x)$ has dropped by 90% of the total drop between the bulk and the pore (Figure 3e)

$$\rho(x_{\rm edge}) = \rho_0 - 0.9(\rho_0 - \rho_{\rm pore})$$
(28)

where ρ_{pore} is the average density inside the pore, and $\rho_0 \approx 1$ g/cm³ is the bulk density of SPC/E water. Since the pore is symmetric about x = 0, the length of the pore is given by $L = 2x_{\text{edge}}$. In the y and z dimensions, the pore region is large enough to encompass all of the water molecules in the pore. The exact size is irrelevant because outside of the pore, molecules come within x_{edge} of the membrane exceedingly rarely.

For both 2d LJ and water simulations, and for each set of parameters, we run 96 simulations. For the water study, we perform simulations at two different currents, 10 and 20 molecules/ns. To calculate p, we fit ΔP versus q using all 96 data points at both currents by linear least-squares fitting with zero intercept, and substitute the slope of the best-fit line for $q/\Delta P$ in eq 27. The error bars in Figures 9–11 correspond to the standard deviations of the best-fit slopes.

All of the simulations are done with the LAMMPS package.⁸⁸ Our implementation of GD is publically available through LAMMPS as fix flow/gauss. We use the VMD and Tachyon packages to generate the simulation snapshots.^{89,90}

3. RESULTS AND DISCUSSION

3.1. Validation of GD: 2d LJ Simulations. The GD method requires that one has a self-consistent definition of the temperature. This definition requires that the local velocity in the fluid separates into a streaming part and a fluctuating thermal part (eq 2). In Figure 4, we show that these two requirements hold over many decades in the Gaussian velocity distribution.

To further validate GD, we compare it to the pump method using two different 2d systems, planar Poiseuille flow and flow through a porous wall (Figure 5a,b). Unlike ref 40, where the porous wall system was studied in detail, our goal is not an exhaustive understanding of these 2d systems. Instead, we use them to illustrate some of the similarities and differences between GD and the pump method. In the context of nonequilibrium statistical mechanics, GD is a constant current protocol, or a Norton ensemble method.⁶³ The pump method is its conjugate Thévenin ensemble, or fixed gradient method. That is, in GD, one applies a fixed current and measures the



Figure 4. Probability distributions of the lab-frame velocity in the *x* and *y* directions for a 2d LJ system at steady state in GD. The flow is in the *x* direction. Both components are Boltzmann distributed (black) over several decades, and the *x*-component is centered at the streaming velocity. This illustrates the self-consistent separation between the thermal and streaming velocities used to define the temperature (eq 2).

resulting pressure drop, whereas in the pump method, one applies a pressure drop and measures the resulting current. Both methods allow all other relevant fields to develop naturally. However, the spatial discontinuity in the pump method's force field leads to some differences in these fields betweem the two methods (Figure 5). The effects of the discontinuity can be emphasized by plotting the relevant spatial profiles across the periodic boundary, where the pump region lies (Figure 6). Because they are conjugate methods, one expects that at the same mass flux, they will both predict the same pressure drop, and vice versa. At the same mass flux (Figure 5c,d), the pressure profiles are clearly different (Figure 5e,f). This is simply because the pump method and GD simulate different physical situations. When the pressure profiles are adjusted according to eq 31, they are nearly identical (Section 3.2 and Figure 7a). The density and temperature profiles, on the other hand, are different (Figure 5g-j). It is not surprising that the differences are the largest in the pump region, but perhaps unexpectedly, the differences extend throughout the entire bulk fluid. The system is heated in the pump region, and this heat influences the entire system (Figure 6).

3.2. Pressure Profile Adjustment and Pressure Drops. To make comparisons between the pressure profiles computed



Figure 5. Comparison of the pump method (blue lines) and GD (black lines) in two different geometries, planar Poiseuille flow (left), and flow through a porous wall (right), both in 2d. Panels (a) and (b) show snapshots from the simulations. The wall atoms are black and the fluid atoms are blue. The flow is in the +*x* direction. We compare the flux (c,d) and the intensive thermodynamic variables, pressure (e,f), density (g,h), and temperature (i,j). The simulations are all at the same mass flux and are at steady state (c,d). The pressure profiles (e,f) must be adjusted according to the discussion in Section 3.2 before being used to compute permeabilities. For porous wall flow, the pump region introduces a discontinuity that has lasting effects on the density (h) and temperature (j) far from the pump region. The densities (g,h) are normalized by the bulk fluid density, ρ_0 , with $\Delta \rho = \rho - \rho_0$.



Figure 6. The same density and temperature profile for the simulation shown in Figure 5h,j. The boundaries are periodically shifted so that the pump region (orange) is centered in the figure at $x = 200 \sigma$, as shown in the simulation snapshot at the top. The effects of the pump region are clearly visible throughout the entire simulation, even though the pump region is almost two orders of magnitude smaller than the simulation box length. The pore and its periodic replica are centered at $x = 0 \sigma$ and $x = 400 \sigma$.



Figure 7. (a) The unadjusted GD pressure profile, $P_{\rm IK1}(x)$ (dotted black), the adjusted GD pressure profile, $P_{\rm IK1}(x) + P_{\rm adj}(x)$ (solid black), and the pump method pressure profile, $P_{\rm IK1}(x)$ (blue), from simulations of flow through a porous wall. (b) The adjusted GD pressure profile for flow through a porous wall (black and gray). To compute the pressure drop, we fit the pressure profile on each side of the pore to a line (orange) and extrapolate that line to the edge of the pore (dashed black, see text). For the purposes of fitting, the pressure profile within 19 σ of the wall is discarded (gray). The pressure drop, ΔP , is then computed as shown by the annotation.

from GD and the pump method, one must make an adjustment to the GD pressure profile, as described here. Consider the hydrodynamic momentum conservation equations for GD and the pump method. In the pump method, far enough from the pump region, we have a fluid moving under a constant applied pressure gradient $\nabla P_{app}(\mathbf{r})$. The momentum conservation equation is⁶³

$$\rho(\mathbf{r}, t) \frac{\mathrm{D}\mathbf{u}(\mathbf{r}, t)}{\mathrm{D}t} + \nabla \cdot \mathbf{P}(\mathbf{r}, t) = -\nabla P_{\mathrm{app}}(\mathbf{r})$$
(29)

where **P** is the pressure tensor, and $\frac{D}{Dt}$ is a total time derivative. In GD, the fluid moves under an external applied acceleration $-\mathbf{I}(t)$, which is uniform in space and fluctuating in time. The momentum conservation equation is⁶³

$$\rho(\mathbf{r}, t) \frac{\mathrm{D}\mathbf{u}(\mathbf{r}, t)}{\mathrm{D}t} + \nabla \cdot \mathbf{P}(\mathbf{r}, t) = -\rho(\mathbf{r}, t)\mathbf{I}(t)$$
(30)

Equations 29 and 30 are the equivalents of Newton's law for a fluid, where the terms on the right-hand side of the equality are the external forces, and $\nabla \cdot \mathbf{P}$ arises from the internal forces. The pressure profile measured in a simulation is the sum of an internal pressure and an applied pressure $P(\mathbf{r}) = P_{\text{int}}(\mathbf{r}) + P_{\text{app}}(\mathbf{r})$, where $P_{int} = Tr(\mathbf{P})/d$, and *d* is the dimensionality of the system. The full hydrodynamic description of a system is contained in $\rho(\mathbf{r}, t)$, $\mathbf{u}(\mathbf{r}, t)$, and $\mathbf{P}(\mathbf{r}, t)$, so when the hydrodynamics are identical, $P_{int}(\mathbf{r})$ is the same for GD and the pump method. But, the applied pressure $P_{app}(\mathbf{r})$ is zero in GD, whereas in the pump method it is nonzero. Thus, the pressure profiles measured with GD and the pump method will be different, even when the hydrodynamics are the same. To compare the pressure profiles generated by the two methods, we require that identical hydrodynamic situations yield the same pressure profiles. We achieve this by adding an adjustment term $P_{adi}(\mathbf{r})$ to the GD pressure profile. We enforce that the hydrodynamics are the same by setting the left-hand sides of eqs 29 and 30 equal

$$\nabla P_{\text{app}}(\mathbf{r}, t) = \rho(\mathbf{r}, t)\mathbf{I}(t)$$
(31)

The pressure adjustment comes from the requirement $\nabla P_{adj} = \nabla P_{app}$ in eq 31. We emphasize that this is an adjustment applied to the data generated in a GD simulation, not a pressure that is applied during a GD simulation. To find the pressure profile adjustment, we integrate eq 31

$$P_{\rm adj}(x, t) - P_{\rm adj}(-L_x/2, t) = I_x(t) \int_{-L_x/2}^x \rho(x', t) \, \mathrm{d}x'$$
(32)

where we have set $\mathbf{I} = (I_x, 0, 0)$, as is the case in our simulations. Because only gradients in pressure drive flow, we can set $P_{\rm adj}(-L_x/2, t) = 0$. This translation to an absolute pressure is a choice of gauge. The result is

$$P_{\rm adj}(x, t) = I_x(t) \int_{-L_x/2}^x \rho(x', t) \, \mathrm{d}x'$$
(33)

where L_x is the length of the simulation box in the *x* direction. The lower bound of the integral $-L_x/2$ is the left edge of the simulation box. Because the box is periodic in the *x* direction, the choice of this lower bound is arbitrary. When the density is approximately constant, as it is in our simulations (Figure 5g,h), the pressure adjustment can be approximated as

$$P_{\rm adj}(x, t) \approx I_x(t)\rho(x, t)x$$
 (34)

which is the form of the equation that we originally used in ref 40. Note that when the flow is in the +x direction, $I_x(t)$ is negative, on average, but the applied acceleration $-I_x(t)$ is in the positive direction. Equation 34 is equivalent to the hydrostatic pressure generated by a gravitational field -I. This hydrostatic pressure should be removed from the calculated pressure because the pressure tensor only depends on internal forces. Previous work has not applied this adjustment, resulting in erroneous reports of disagreement between the pump method and other methods.^{43,78}

This discussion presupposes that the hydrodynamics in the pump method and GD can be made equivalent. In a simulation large enough to equilibrate the local pressure jump and sudden gradients in other intensive thermodynamic variables that the pump method generates, GD and the pump method would generate equivalent hydrodynamics. But for finite simulations, even very large ones, we find that this does not hold (Figure 6).

We compute the pressure profile using the zeroth-order Irving–Kirkwood approximation^{91,92} (IK1) and add the pressure adjustment (eq 34) to it $P(x) = P_{IK1}(x) + P_{adj}(x)$. We discard the pressure profile within 19 σ of the wall atoms because the IK1 method is only valid in homogeneous fluids (Figure 7b).^{91,92} Used in this way, the IK1 method is convenient and accurate, but not unique.^{91–95} We use the pressure profile to compute the pressure drop across a porous membrane ΔP , which we use to calculate the permeability of the pore with eq 27. However, ΔP is a macroscopic quantity, which we compute from microscopic simulation data by extrapolating the pressure profile in the bulk fluid to the edges of the pore (Figure 7b). This definition of ΔP gives good agreement between GD and the pump method at low *Re.*⁴⁰

The pressure profiles shown in Figures 5e,f and 7 are time averaged. The time average of eq 34 is

$$\overline{P_{\text{adj}}(x,t)} \approx -\overline{I_x(t)\rho(x,t)}x$$
(35)

where an overbar denotes a time average. Here, we use the approximate eq 34 for simplicity, but all of the following results easily generalize to eq 33. In principle, the time dependence of $I_x(t)$ does not decouple from the time dependence of $\rho(x, t)$, but in practice, fluids at high densities are incompressible so that the fluctuations of $\rho(x, t)$ are small. Therefore, we can make the approximation

$$\overline{P_{\text{adj}}(x, t)} \approx -\overline{I_x(t)} \cdot \overline{\rho(x, t)} x$$
(36)

which can simplify simulation data output and save storage space. Use of eq 35 would require either the output of $I_x(t)$ and $\rho(x, t)$ at every sample time step or the premeditated on-the-fly computation of $\overline{I_x(t)\rho(x, t)}$. Alternatively, eq 36 only requires the output of a single time-averaged profile, $\overline{\rho(x, t)}$, and the scalar time average, $\overline{I_x(t)}$.

3.3. Slip Length. Continuum hydrodynamics cannot be trusted on atomistic length scales, but here we use it on systems large enough that a continuum approximation should be accurate. In hydrodynamic models, the microscopic interactions between the fluid and the walls of the system give rise to boundary conditions. In ideal hydrodynamics, the velocity of the fluid goes to zero at the fluid—solid boundary. This is the so-called no-slip boundary condition on the velocity. Figure 8a shows that GD generates the parabolic velocity profile that continuum hydrodynamics predicts, but the no-slip boundary condition is not satisfied. The deviation from no-slip behavior is

Article



Figure 8. The slip length L_s from GD simulations of a 2d LJ fluid in steady-state planar Poiseuille flow. (a) The *x*-component of the velocity profile along *y*, $u_x(y)$ (blue), is fit to a parabola (red). We take a linear extrapolation of the parabolic fit to the vertical intercept $u_x = 0$ (purple). L_s is the distance between the edge of the pipe (black) and the vertical intercept. The inset shows a close-up of the region in the light green box. (b) L_s is an order of magnitude larger with rigid walls (blue) than with flexible walls (red and yellow). When the walls are flexible, we thermostat the system through either the walls (yellow) or the fluid (red), but not both.

quantified by the size of the slip length $L_{\rm s}$, as defined by Kannam et al.⁴⁹ and illustrated in Figure 8a.

In carbon nanotubes, water passage rates have been observed in simulations^{45–51} and experiments^{50,96–99} that are much faster than the no-slip Hagen–Poiseuille predictions. This is thought to be the result of almost frictionless flow, which gives rise to very large slip lengths. However, estimates of the slip length and the flow enhancement vary by several orders of magnitude among both experiment and simulation.⁴⁹ The disagreement of simulation results is, at least in part, likely due to the wide variety of water models and surface–water potentials used, as well as the rigidity of the surface.^{44–46,100–104} Another important aspect is the type of thermostat used in the simulations, which can affect the measured slip length.^{49,104,105} Here, we use the simple 2d LJ fluid as a test system to study the effects of wall rigidity and thermostatting. When the walls are rigid, the system can only be thermostatted through the fluid. When the walls are flexible, however, either the walls or the fluid can be thermostatted.

In the rigid wall simulations, the wall atoms are fixed in space. In the flexible wall simulations, the wall atoms are harmonically bound to their initial position \mathbf{r}_0 by the potential $U(\mathbf{r}) = K(\mathbf{r} - \mathbf{r}_0)^2/2$ with $K = 25 \epsilon/\sigma^2$. This value of K is large enough to prevent fluid atoms from penetrating the wall but small enough to allow significant energy transfer between the wall and the fluid. We place an extra layer of fixed wall

atoms behind the harmonic ones to stop the few fluid atoms that do penetrate the wall. We also place an extra layer of atoms behind the rigid wall, for consistency with the flexible walls. In all of the other simulations presented in this article, the walls are rigid, and there is only one layer of wall atoms. We find that $L_{\rm s}$ is an order of magnitude larger on rigid walls (Figure 8b). This is because the flexible walls can absorb kinetic energy from the fluid, whereas the rigid walls cannot. With flexible walls, $L_{\rm s}$ is smaller than the radius of an atom, so the flow is effectively no-slip. We also measure $L_{\rm s}$ as a function of the Reynolds number

$$Re = \frac{u_{\max}h\rho_0}{\eta}$$
(37)

where u_{max} is the maximum velocity in the flow, $h = 30 \sigma$ is the distance between the walls, ρ_{0} = 0.8 σ^{-2} is the bulk fluid density, and $\eta \approx 2.2 \ \epsilon \tau / \sigma$ is the bulk viscosity measured at equilibrium using the Green-Kubo relation.⁶⁵ We find no evidence of the divergence of η that others have reported for the diffusion constant in two dimensions.^{106–108} We tune *Re* by increasing the flux through the channel, thereby increasing u_{max} . For reference, Re = 25 corresponds to a mass flux of about $J = 1 m/\sigma\tau$, and a shear rate of about $\dot{\gamma} = 0.15 \tau^{-1}$. When the walls are flexible, we thermostat the system through either the fluid or the walls. When the fluid is thermostatted, L_s increases as a function of Re (Figure 8b), a trend that has been observed before in simulations.^{49,109} When the wall atoms are thermostatted instead of the fluid, L_s changes only slightly but the qualitative trend is reversed at high Re (Figure 8b). The slip length averages very slowly, especially in nonequilibrium simulations,⁴⁴ so this discrepancy may not be statistically significant but would be an interesting topic for future study. Both the wall rigidity and application of the chosen thermostat could be a factor in the large scatter of simulation and experimental slip lengths in carbon nanotubes.⁴⁵

3.4. Tuning the Hydrophobicity. The bulk hydrophobicity, measured by the wetting contact angle that a droplet of water forms on a surface, is a macroscopic manifestation of the microscopic interactions between the surface and the water. These interactions can be divided into two categories: the interactions between the surface and the polar degrees of freedom in the water, and the interactions between the surface and the density degrees of freedom in the water, or van der Waals interactions. In a previous publication,⁴⁰ we studied the permeability of water as a function of the voltage applied to a graphene sheet. The resulting electric field couples strongly to the polar degrees of freedom in water. In this section, we focus on the role of the van der Waals interaction between a model membrane and water. This separation between polar and van der Waals interactions is a conceptual device consistent with qualitative classes of intermolecular forces; it does not translate to a rigorous separation between the density and polar degrees of freedom in the liquid on all length scales. The statistics of density and polarization fields in liquid water are coupled, so tuning ϵ will have an impact on polarization fluctuations, just as changing the voltage will modify the density fluctuations.

The contact angle is incredibly sensitive to changes in both types of interactions. Previous simulations from our group predicted that changing the voltage relative to the Fermi level by only ± 0.35 V decreases the contact angle by almost 20° .¹¹⁰ This is an electrowetting effect completely dominated by collective polarization fluctuations.¹¹⁰ Experimental work is

consistent with these predictions.^{111,112} The contact angle is likewise sensitive to changes in the van der Waals interaction strength. A $0.2k_{\rm B}T$ change in the LJ ϵ parameter, which tunes the van der Waals interactions between the membrane atoms and the water, changes the contact angle by 130° .⁸⁶ In previous work, we examined in detail how electrical doping changes water transport through porous graphene.⁴⁰ In this work, we focus our attention on how van der Waals interactions and pore functionalization impact transport. Because a characteristic trait of liquid water is its ability to form extended hydrogen bonding networks, we also perform simulations with a model we call "apolar water", which has the same mass, density, and steric interactions as the SPC/E water model but has no hydrogen bonds or polar degrees of freedom.

3.4.1. van der Waals Interactions. We first discuss the results of tuning the van der Waals part of the hydrophobicity through the LJ ϵ parameter. We find that, as the atomic membranes become more hydrophobic, the permeability first increases slowly and then drops sharply (Figure 9a). The most noticeable part of the data in Figure 9a is the sharp drop in permeability, which occurs at different critical contact angles for single- and double-layer atomic membranes. As we show below, the thermodynamics of wetting describe this threshold behavior.

Just as the application of hydrodynamics to atomically small length scales is specious, so is the application of macroscopic thermodynamics, and for the same reasons. Nonetheless, we show that the thermodynamics of the dewetting transition gives a semiquantitative description of the threshold phenomenon observed for the permeability of hydrophobic atomic membranes (Figure 9a). The dewetting transition is an equilibrium phenomenon that shares some similarities to homogeneous nucleation theory and capillary action. An early observation of the dewetting transition using computer simulations comes from the work of Wallqvist and Berne, who studied the spontaneous evaporation of liquid water between two paraffin plates.¹⁷ The free energy of dewetting is a competition between bulk and surface terms associated with filling or emptying the pore.⁵⁷

The pore in both single- and double-layer atomic membranes is roughly cylindrical. For a cylindrical pore with radius r and length L_i consider the grand potential of the pore when it is occupied by liquid Ω_i or vapor Ω_v^{24}

$$\Omega_l = -P_l \,\pi r^2 L + 2\gamma_{sl} \,\pi r L \tag{38}$$

$$\Omega_{\rm v} = -P_{\rm v}\pi r^2 L + 2\gamma_{\rm sv}\pi r L + 2\gamma_{\rm vl}\pi r^2 \tag{39}$$

where P_v and P_l are the pressures of the respective phases, and γ_{sv} , γ_{sl} , and γ_{vl} are the surface tensions. The free-energy difference between the phases is

$$\Delta \Omega \equiv \Omega_{\nu} - \Omega_{l} = \Delta P_{\rm ph} \pi r^{2} L + 2 \gamma_{\nu l} \pi r L \cos \theta + 2 \gamma_{\nu l} \pi r^{2}$$
(40)

where $\Delta P_{\rm ph} \equiv P_l - P_v$ is the pressure difference between the phases, and θ is the contact angle from Young's equation, $\gamma_{vl} \cos \theta = \gamma_{sv} - \gamma_{sl}^{32}$ At the critical contact angle, $\Delta \Omega = 0$, which gives the relationship for the critical contact angle θ_c

$$-\cos\theta_{\rm c} = \frac{\Delta P_{\rm ph}r}{2\gamma_{\rm vl}} + \frac{r}{L}$$
(41)

Using the approximate values $\Delta P_{\rm ph} = 1$ atm and $\gamma_{\rm vl} = 72.1$ mJ/m², we find



Figure 9. (a) Permeability as a function of contact angle on singlelayer (blue) and double-layer (red) atomic membranes. We tune the contact angle by changing the membrane–water LJ interaction energy ϵ .⁸⁶ As the membranes become more hydrophobic, the permeability initially increases due to decreasing friction and then decreases sharply due to dewetting. The arrows show the critical dewetting contact angles from macroscopic thermodynamics for both single-layer (dark red) and double-layer (light blue) membranes, reported in Table 1. (b) No dewetting transition is seen for apolar water because this model does not form a hydrogen bonding network. We report the LJ ϵ parameter as the "effective" contact angle to make a connection to (a). The effective contact angle corresponds to the value of ϵ that generates that contact angle for SPC/E water. The improvement factor is the ratio of the permeability to that of conventional RO membranes (see the text).

$$-\cos\theta_{\rm c} = r \left(\frac{1}{1.4\,\mu{\rm m}} + \frac{1}{L} \right) \tag{42}$$

In our simulations, L is on the order of Å, so the first term is negligible and we can simplify the relation to

$$-\cos\theta_{\rm c} \approx \frac{r}{L} \tag{43}$$

The predictions of eq 43 as a function of L for the critical angle on single- and double-layer atomic membranes are summarized in Table 1 and shown as arrows in Figure 9a. These predictions

Table 1.	Predictions	of Eq	uation	43
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	r (Å)	L (Å)	$\theta_{\rm c}$ (°)
single-layer	3.7	4.2	152
double-layer	3.7	6.5	125

are surprisingly good given the macroscopic equilibrium nature of the free-energy argument, but irrespective of their quantitative accuracy, they explain the qualitative decrease in θ_c as the pore gets longer. It is interesting to note that eq 43 predicts that the critical contact angle can never be smaller than 90° . Furthermore, as long as the pore length is significantly smaller than 1 μ m, well within the regime where macroscopic thermodynamics is valid, the critical contact angle only depends on the aspect ratio of the pore and is independent of the properties of the liquid and the membrane. The radius r used in Table 1 is the center-to-center distance between atoms in the geometry shown in Figure 3a,c, and the pore lengths L are determined using eq 28, as discussed there. This choice of rreflects the ambiguity inherent in the thermodynamics behind eq 43. With only a handful of molecules to distinguish between "vapor" and "liquid" phases inside the pore, there can be no rigorous classification of a thermodynamically stable interface in either putative phase. Nonetheless, thermodynamic dewetting calculations can be semiquantitative for nanoscopic volumes.² Since the water density profile inside the pore is hourglass shaped (Figure 3e), an optimal cylinder to approximate the wetted interface for the pore would place r larger than the minimally accessible surface area that compensates for the excluded volume of the membrane atoms in the narrowest region of the channel. We simply use a value of r equivalent to the distance between atomic centers, partly because it is easy to determine from experiments.

The other important feature of the data in Figure 9a is the slow increase in the permeability as the membrane becomes more hydrophobic. This is due to friction between the water and the membrane. On more hydrophilic membranes, the water-membrane interaction is more attractive, so the water molecules stick more strongly to the membrane, leading to more friction and lower permeability. This is a purely dynamical aspect of the passage process and has no counterpart at equilibrium.

While the dewetting transition observed for SPC/E water leads to a threshold behavior at intermediate hydrophobicities, the permeability of apolar water is a smooth and monotonically increasing function of the effective contact angle (Figure 9b). For apolar water, we report the LJ ϵ parameter as the "effective" contact angle to make a connection to SPC/E water. The effective contact angle corresponds to the value of ϵ that generates that contact angle for SPC/E water according to ref 86. We speculate that the lack of a dewetting transition in apolar water is due to the low vapor pressure and high surface tension of SPC/E water compared to apolar water. Because water forms hydrogen bond networks, it has a remarkably low vapor pressure and high surface tension for a low molecular weight substance. These features make the approximation in eq 43 accurate for water. Apolar water cannot form hydrogen bonds, so it is far from liquid-vapor coexistence and its dewetting transition over this range of ϵ . Removing the dewetting transition simplifies the analysis of the permeability because apolar water only experiences friction.

The dewetted pores also reveal a key difference between the pump method and GD. GD fixes the current but admits fluctuations in the pressure drop. The pump method is the complementary method to GD, as it fixes the pressure drop but admits fluctuations in the current. For very small currents, flow becomes intermittent and equilibration to steady state very difficult. This gives rise to a discrepancy between the pump method and GD on very hydrophobic membranes (Figure 10).



Figure 10. The permeability of a porous double-layer atomic membrane as a function of contact angle on a single-layer membrane. The pump method (blue) and GD (black) show the sharpest disagreement for the most hydrophobic membranes (circled in red), past the dewetting transition. The improvement factor is the ratio of the permeability to that of conventional RO membranes (see the text).

To allow sufficient passage to achieve steady state, one must apply exceedingly high pressures in the pump region. At very high pressures, it is not computationally feasible to converge the results with respect to the box length. Although GD will also generate large pressures to maintain a given current, the external acceleration is not discontinuous as in the pump method, so shorter boxes can be used. Further, GD allows the user to specify how many passage events they want to observe in a simulation of a given length, and automatically finds the pressure drop that is necessary to generate that current. Practically, this eliminates the need for preliminary testing with the pump method to determine the pressure required to drive sufficient flow.

3.4.2. Pore Functionalization: Local versus Nonlocal Polar Interactions. In previous work, we tuned the hydrophobicity of porous graphene through electrical doping and studied its effect on water transport.⁴⁰ We applied a voltage to the graphene by charging the carbon atoms,^{40,110} which is an experimentally realizable technique for tuning the hydrophobicity of graphene.^{111–116} We found that the bulk equilibrium hydrophobicity is not predictive of the permeability.⁴⁰ Instead, the changes in permeability are governed by a shift in the molecular transport mechanism: from a translocation mechanism, where the water molecules move through the pore in an unbroken chain, to an evaporation–condensation mechanism, where individual water molecules evaporate from the bulk on one side of the membrane and condense on the other side.⁴⁰ Ref 40 argues that it is the local interactions between the pore and the water inside the pore that are responsible for this shift in mechanism.

Here, we tune only these local interactions through a simple model for chemical pore functionalization. Instead of studying a slew of possible chemical modifications to the pore edge, we model the effect by simply charging the carbon atoms at the edge of the pore (Figure 11, inset). Although this is surely not exhaustive, it gives an idea of the trends in permeability that might be discovered with chemically modified graphene pores. We report the applied charge as an "equivalent voltage" to



Figure 11. The permeability of porous single-layer graphene as a function of applied voltage (black points),⁴⁰ compared to the permeability (red points) when only the carbon atoms on the edge are charged (red atoms, inset). This no longer corresponds to an applied voltage, so we report it as an "equivalent voltage." The charge per carbon atom on the edge of the pore is equivalent to what it would be in a fully doped graphene sheet at an equivalent voltage. The trend is the same whether the entire membrane is charged or only the edge atoms are charged, reinforcing the evaporation–condensation mechanism facilitated by local hydrogen bonding, proposed in ref 40. The improvement factor is the ratio of the permeability to that of conventional RO membranes (see the text).

make contact with the work in refs 110 and 40, where an applied voltage was modeled by charging the graphene sheet according to the dispersion relation of graphene, and the excess charge was distributed equally between all of the carbon atoms. Here, at a given equivalent voltage, the charge on an edge carbon atom is equal to the charge per carbon atom at that voltage in refs 110 and 40, but the other carbon atoms are neutral.

We find that the trend in permeability is qualitatively unchanged whether a voltage is applied to the sheet, tuning the bulk hydrophobicity, or only the local interactions are tuned, modeling pore functionalization (Figure 11). This supports the hypothesis presented in ref 40 and discussed above that the shift in molecular transport mechanism responsible for the observed permeability trend is dominated by the local interactions between the water molecules and the pore. In other words, the molecular interactions in the vicinity of the pore overpower the collective polarization fluctuations in the bulk liquid. These local interactions could be tuned experimentally through pore functionalization, providing a useful handle for optimizing graphene membranes and other atomically thin membranes. Note that the trend is slightly weaker when only the edge carbon atoms are charged (Figure 11). This is likely because the next ring of carbon atoms around the pore also contributes to the local interactions, but were not charged in this study. The general behavior we observe here when tuning the polar part of the hydrophobicity is qualitatively different from that seen when tuning the hydrophobicity through the van der Waals interactions (Figure 9a). The effects of friction and dewetting, which were central to the behavior observed in Section 3.4.1, are overshadowed here by the molecular transport mechanism. On detailed inspection, the

contact angle alone is insufficient to fully characterize even the thermodynamic aspects of the hydrophobic effect; ref 117 also finds discrepancies between polar and nonpolar hydrophobicity in the statistics of interfacial fluctuations.

3.5. Bursty Transport. An interesting observation in these systems is that the passage time series appears bursty, especially on the most hydrophobic membranes (Figure 12). The passage



Figure 12. The net number of passage events as a function of time for single-layer 2d crystals, n(t) (see the text), transitions from a normal biased random walk in the most hydrophilic membrane (blue) to a transport process dominated by bursts and long pauses in the most hydrophobic membrane (red).

time series is the net number of molecules that have passed through the pore as a function of time. We compute the passage time series using the collective variable n(t) defined by Zhu et al. (eq 24).⁴¹ The traces in Figure 12 are the time series n(t), which are computed using the pore region defined in Figure 3e according to eq 28 and the equilibrium density considerations discussed there.

3.5.1. CTRW Model. To understand the bursty behavior observed in Figure 12, we use a biased CTRW model, where a forward passage event is like a hop to the right on a 1d lattice, and a backward passage event is a hop to the left (Figure 13a). This model is a one-step Markovian process in a discrete state space. To map the continuous n(t) onto this discrete state space, we must discretize it. This can be done with varying complexity, but the simplest method of rounding to the nearest integer is adequate (Figure 13b). We test that the discretization procedure does not corrupt the data by checking that both n(t)and the discretized n(t) have the same mean-squared displacement at equilibrium and therefore yield the same collective diffusion coefficient.⁴¹ The dynamics of an unbiased CTRW are completely determined by the waiting-time distribution $\psi(t)$, which is the probability of observing a given waiting time between two consecutive hops, or passage events. For this system, the CTRW is biased because there is a net forward flux, so we must consider the forward and backward waiting-time distributions separately, $\psi_{\rm f} \neq \psi_{\rm h}$ (Figure 13a). We compute the waiting times from the discretized n(t)as the elapsed time between each pair of consecutive passage events. The forward waiting times are those where the waiting time is terminated by a forward passage event, and likewise for the backward waiting times.

We plot the complementary cumulative waiting-time distributions to avoid errors associated with binning (Figure 13c,d).¹¹⁸ The complementary cumulative probability

$$\Psi_{\rm f}(t) = 1 - \int_0^t {\rm d}t' \, \psi_{\rm f}(t') \tag{44}$$

is the probability that there is no hop by time t. For brevity, we refer to $\Psi_{\rm f}(t)$ as the complementary probability. We find that the forward waiting-times appear to be power-law distributed for a couple of decades on the most hydrophobic membranes (Figure 13c) but are exponentially distributed on the hydrophilic membranes (Figure 13d). Note that for a power-law distribution $\psi(t) \sim t^{-\alpha}$, the complementary distribution is also power law, with an exponent that is shifted by one $\Psi(t) \sim t^{-\alpha+1}$, so plots of either the distribution or the complementary distribution can be used to identify power-law behavior.

3.5.2. *MLE*. To characterize and quantify the power-law behavior, we fit the waiting-time distributions ψ_f to a series of model distributions: power-law, power-law with exponential cutoff (power-law-exp), exponential, biexponential, stretched-exponential, and log-normal. The power-law-exp distribution is defined as

$$\psi_{\rm f}(t) \sim t^{-\alpha} \, {\rm e}^{-\beta t} \tag{45}$$

with the appropriate normalization factor. Unlike the pure power-law distribution, the complementary distribution to the power-law-exp distribution is not power-law-exp. Instead, it is an upper incomplete gamma function

$$\Psi_{\rm f}(t) \sim \Gamma(1 - \alpha, \beta t) \tag{46}$$

which behaves asymptotically as $t^{-\alpha+1}$ for $\beta t \rightarrow 0$, and as $t^{-\alpha} e^{\beta t}$ for $\beta t \rightarrow \infty$. So, although the complementary distribution of a power-law-exp distribution is not exactly power-law-exp, it asymptotically converges to a power-law-exp distribution for large and small βt . One can find a probability distribution for which the complementary distribution is exactly power-law-exp

$$\psi_{\rm f}(t) \sim t^{-\alpha} \,\mathrm{e}^{-\beta t} (1 - \alpha - \beta t) \tag{47}$$

We also fit the data to this distribution, which is equivalent to fitting the complementary probability $\Psi_{\rm f}$ to a power-law-exp distribution.

We use the MLE method to find the best-fit parameters for each of these models. This gives significantly less biased estimates of the best-fit parameters than least-squares fitting methods.¹¹⁸ For the power law, exponential, and log-normal distributions, there are closed-form solutions for the MLE parameters. For the other distributions, we numerically maximize the likelihood. The power-law and power-law-exp distributions diverge at t = 0, so they must have some shorttime cutoff t_c below which they do not apply (Figure 14a). MLE cannot be used to find this cutoff parameter because as t_c changes, the data set changes size. Instead, we numerically minimize a Kolmogorov-Smirnov statistic D to find the optimum t_c . Because we are interested in the behavior of the tail of the distribution, we use the Anderson-Darling statistic, which is weighted to be equally sensitive over the entire domain of the distribution

$$D = \max_{t > t_c} \frac{|\Psi(t) - \Psi(t)|}{\sqrt{\hat{\Psi}(t)(1 - \hat{\Psi}(t))}}$$
(48)

where $\hat{\Psi}(t)$ is the model distribution with the best-fit parameters from MLE.¹¹⁸ We perform likelihood ratio tests as described in ref 118, which suggest that the power-law-exp distribution is the best model to describe our data of those



Figure 13. (a) We model the passage of water through atomic membranes as a CTRW that brings the system between states of different counts, illustrated in the coarse graining (red line) of the time series n(t) (gray line) in (b). This time series is a segment of that shown in Figure 12. The model is fully described by the forward and backward complementary waiting-time distributions $\Psi_{\rm f}(t)$ and $\Psi_{\rm b}(t)$, the probabilities that no events have occurred either forward or backward, respectively, between time zero and time t. (c) A log-log plot of $\Psi_{f}(t)$ for the most hydrophobic singlelayer membrane (red) shows that it follows a power law over about two decades with an exponential cutoff at long times. A power-law distribution of waiting times is one hallmark of a clogging transition.⁵⁸ The black line shows the power-law part of a fit by maximum likelihood estimation (MLE) to eq 47 (see the text). The power-law exponent is 1.7, which indicates a divergent average waiting time (eq 49). (d) A log-linear plot of $\Psi_{\rm f}(t)$ for the most hydrophilic single-layer membrane (blue) and apolar water on the most hydrophobic single-layer membrane (green) emphasizes the exponential decay. There is no significant power-law relaxation in either of these cases. Note the dramatic difference in the range of the x axis in panels (c) and (d).

listed above but these tests are too noisy to make any conclusive statements in this case. Because eqs 45 and 47 predict the same power-law behavior and lead to the same qualitative conclusions, we henceforth limit ourselves to the case where $\Psi_{\rm f}$ is power-law-exp (eq 47).

3.5.3. Clogging Transition. To summarize the MLE results, we find that on the most hydrophobic membranes, the waitingtime distributions we measure are best fit by a power-law distribution cutoff by an exponential at long times (Figure 13c). On the more hydrophilic membranes, and with apolar water, regardless of the hydrophobicity, a power-law-exp distribution is still a good fit, but the exponential cutoff is at much shorter times, $\beta^{-1} \approx 10$ ps, so that the power-law part of the distribution is never the dominating factor (Figure 13d). On the hydrophobic membranes, the exponential cutoff happens at very long times, $\beta^{-1} \approx 100-200$ ps, much longer than the timescale of any relevant dynamics in water. A power-law distribution of waiting times is characteristic of clogging,⁵⁸ a common phenomena in granular flows.^{58-60,119,120} For a true clogged process, the waiting-time distribution is purely powerlaw at long times, with an exponent $\alpha \leq 2$. This corresponds to a divergent average waiting time

$$\langle t \rangle = \int_{t_c}^{\infty} dt \ t \psi(t)$$

= $\int_{t_c}^{\infty} dt \ t^{1-\alpha} \to \infty \quad \text{if } 0 < \alpha \le 2$ (49)

which corresponds to the intuition of clogging, that once a clog has formed, another passage event will not happen without some external influence. Here, the MLE fits predict $\alpha \approx 1.7$, which, without the exponential cutoff, would correspond to a divergent average waiting time. Without the exponential cutoff, the system would not be able to reach steady state because it would be nonergodic.¹²¹ We postulate that the exponential cutoff is due to the finite size of the system, which limits the maximum wavelength of density fluctuations. Also, because the membrane is atomically thin, the capillary-wave fluctuations may be particularly relevant to transport across the pore. The pore could act as a window function that filters the power-law spectrum of the capillary waves, resulting in the power law with exponential cutoff that we observe.^{21,11}

For clogged processes, the power-law waiting-time distribution should be accompanied by an exponential burst-size distribution. $^{58-62,119}$ The separation in timescales for the hydrophobic sheet in Figure 12 is evident. This time series is punctuated by long pauses and large jumps, or bursts. A burst is a set of events that occur without a pause time greater than t_c



Figure 14. (a) MLE fit (gray line) of eq 47 to the complementary waiting-time distribution on the hydrophobic membrane shown in Figures 12 and 13c (black). The short time cutoff t_c is shown in blue. (b) Any waiting time that is longer than t_c (blue) starts a new burst (red). This shows two bursts of size one and one burst of size four. (c) The burst sizes are exponentially distributed for the same systems shown in Figures 13c,d: SPC/E water on a hydrophilic (blue) and a hydrophobic (red) membrane, and apolar water on a hydrophobic membrane (green). This is another hallmark of a clogging transition.⁵⁸

between consecutive events (Figure 14b).⁵⁸ Figure 14a shows t_c for a particular waiting-time distribution. In our data, t_c is always between 1 and 10 ps. The burst size is the net number of molecules that pass through the membrane during a burst. We find that the burst-size distribution is exponential, as expected for a clogged process (Figure 14c). The burst size can be zero or negative, but Figure 14c only shows the probability for positive burst sizes.

The clogging behavior we observe is commonplace in granular flows but has never to our knowledge been observed in a molecular fluid. This behavior is not unreasonable given that, on the scale of the pore, water *is* granular. The behavior we

observe, however, cannot be explained solely by the granular nature of water on these length scales. If that were the case, we would observe the same behavior for apolar water. Instead, we find no evidence of clogging in apolar water, even on the most hydrophobic membranes (Figure 13d). In granular flows, arch structures form at the opening, causing frustration and clogging.^{58,60,62} Here, we postulate that the hydrogen bonding network in water causes long range frustration that leads to clogging. In apolar water, this long-ranged hydrogen bonding network is not present, so clogging does not take place. It is also possible that hydrogen bonds stabilize arch structures in water that are unstable in apolar water at the same density. Further, our apolar water model is equivalent to a LJ fluid at $T = 3.8 \ \epsilon/k_{\rm B}$ and $\rho = 1.0 \ \sigma^{-3}$ which is deep into the regime of the supercritical fluid phase.¹²² It is tempting to think that the absence of clogging is due to the low viscosity of a supercritical fluid, but in fact, its viscosity is comparable to or higher than that of the dense liquid phase.¹²³

Article

4. CONCLUSIONS

In this work, we employ our nonequilibrium molecular dynamics tool, GD,⁴⁰ to study the hydrodynamics of liquids moving through atomically small spaces. We probe the relationship between microscopic interactions and emergent macroscopic hydrodynamic quantities, such as the slip length, channel permeability, and friction. These quantities are often material-specific inputs into hydrodynamic transport theories, and understanding their origin is critical for tailoring the chemistry of intermolecular interactions to control fluid flow on atomic and nanoscale dimensions. GD is a tool that may shed light on many interesting processes, but we focused our attention on understanding how water flows through porous 2d crystals because it is a process fundamental to next-generation RO membranes. 36,37,39,52

We show that GD is capable of satisfying expectations for velocity distributions from statistical mechanics, and, when the atomic degrees of freedom can be sensibly coarse-grained into a continuum description, it reproduces results consistent with hydrodynamics. We compare the results of GD to those of a closely related technique called the "pump method"⁴³ for large simulations of simple 2d liquids in two different flow scenarios, planar Poiseuille flow and flow through a porous wall. In earlier work, we showed that these two methods give very similar results for the permeability of a channel at low Reynolds number.⁴⁰ Here, we report that the nonequilibrium spatial distributions of intensive thermodynamic variables, such as temperature and density, can be different between these two methods. This means that other transport behaviors, such as heat transport, might be significantly different between these two methods. It also calls into question the assumption of local equilibrium.^{63,66} As far as hydrodynamic quantities are concerned, we find that the slip length can vary by an order of magnitude if the solid surface in contact with the fluid is rigid or if it is flexible. This observation connects to controversies in the literature about the slip length of water in carbon nanotubes and calls for further systematic investigation,^{44-51,96-99,101-104} though we do not endorse the concept of a slip length for single-file water as being even conceptually accurate. It will require further work to understand the effects of membrane flexibility and thermostatting in porous graphene simluations as well.

The wetting contact angle is the most convenient measure of a substance's hydrophobicity, and here we use the wetting

contact angle as a surrogate for the hydrophobicity. The contact angle is sensitive to the liquid-solid surface tension, and there are several equivalent ways to tune the surface tension that differ in their microscopic details. Doping a graphene sheet with electrons or holes both decrease the contact angle, yet the permeability is a monotonically decreasing function of the sheet's charge.^{40,110} In this work, we mimic the effect of changing a membrane's chemical composition by tuning the van der Waals interaction strength between membrane atoms and the water molecules in electrically neutral single- and double-layer membranes. Small changes of the LJ c parameter, on the order of fractions of $k_{\rm B}T$, lead to dramatic changes in both the wetting contact angle and the permeability of atomic membranes. Just like charged membranes, the permeability is not a simple function of the contact angle. Although the contact angle does not predict the permeability, the thermodynamic theory of dewetting does predict the observed onset of a threshold in the permeability.²⁴ The permeability increases dramatically if there is a thermodynamic driving force for the pore to wet, suggesting a tenuous connection to capillary action in this system. Once the pore wets, increasing the strength of the van der Waals attractions between the membrane and the water increases the friction and decreases the permeability. This competition, between the static hydrophobicity that drives wetting and the dynamical hydrophobicity that modulates friction, produces a "Goldilocks zone" for the optimum permeability as a function of the hydrophobicity of neutral atomic membranes. From a practical perspective, for membranes that are much less than 1 μ m in length, the optimal contact angle can simply be estimated from the aspect ratio of the channel in the membrane.

Finally, we find qualitative differences between the most hydrophilic and hydrophobic membranes for the statistics of water passage. In the extremely hydrophobic cases, water moves across the membrane in a series of fits and starts, punctuated by long pauses and rapid bursts. A continuous-time, one-step Markov model of the process shows that the waiting-time distribution exhibits a power-law decay over about two decades in time, from about 1-100 ps, with an exponential cutoff. The burst-size distribution exhibits an exponential decay. These two features, a power law in the waiting-time distribution and an exponential distribution of burst sizes, are both hallmarks of the clogging transition observed in a wide variety of systems, including driven granular flows.^{58-62,119} The clogging we observe here, however, cannot be attributed entirely to the granular nature of water on these atomic length scales because it is absent in "apolar water," a simple liquid that has the same mass, density, temperature, and van der Waals parameters as SPC/E water, but no charges. Because apolar water cannot form hydrogen bonds, we postulate that the frustrated transport of water through very hydrophobic membranes is rooted in its hydrogen bond network rather than the kind of geometrical or steric crowding one observes in granular systems.

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REFERENCES

(1) Chandler, D. Interfaces and the Driving Force of Hydrophobic Assembly. *Nature* **2005**, *437*, 640–647.

(2) Patel, A. J.; Garde, S. Efficient Method To Characterize the Context-Dependent Hydrophobicity of Proteins. J. Phys. Chem. B 2014, 118, 1564–1573.

(3) Xi, E.; Patel, A. J. The Hydrophobic Effect, and Fluctuations: The Long and the Short of it. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*, 4549–4551.

(4) Li, I. T. S.; Walker, G. C. Signature of Hydrophobic Hydration in a Single Polymer. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 16527– 16532.

(5) Davis, J. G.; Gierszal, K. P.; Wang, P.; Ben-Amotz, D. Water Structural Transformation at Molecular Hydrophobic Interfaces. *Nature* 2012, 491, 582–585.

(6) Zhou, R.; Huang, X.; Margulis, C. J.; Berne, B. J. Hydrophobic Collapse in Multidomain Protein Folding. *Science* **2004**, *305*, 1605– 1609.

(7) Baldwin, R. L. Temperature Dependence of the Hydrophobic Interaction in Protein Folding. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 8069–8072.

(8) Tanford, C. The Hydrophobic Effect and the Organization of Living Matter. *Science* 1978, 200, 1012–1018.

(9) Stillinger, F. H. Water Revisited. Science 1980, 209, 451-457.

(10) Zhang, X.; Zhu, Y.; Granick, S. Hydrophobicity at a Janus Interface. *Science* **2002**, *295*, 663–666.

(11) Petersen, C.; Tielrooij, K.-J.; Bakker, H. J. Strong Temperature Dependence of Water Reorientation in Hydrophobic Hydration Shells. *J. Chem. Phys.* **2009**, *130*, No. 214511.

(12) Buchanan, P.; Aldiwan, N.; Soper, A. K.; Creek, J. L.; Koh, C. A. Decreased Structure on Dissolving Methane in Water. *Chem. Phys. Lett.* **2005**, *415*, 89–93.

(13) Laage, D.; Stirnemann, G.; Hynes, J. T. Why Water Reorientation Slows Without Iceberg Formation Around Hydrophobic Solutes. J. Phys. Chem. B **2009**, *113*, 2428–2435.

(14) Raschke, T. M.; Levitt, M. Nonpolar Solutes Enhance Water Structure Within Hydration Shells While Reducing Interactions Between Them. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 6777–6782.

(15) Matysiak, S.; Debenedetti, P. G.; Rossky, P. J. Dissecting the Energetics of Hydrophobic Hydration of Polypeptides. *J. Phys. Chem. B* **2011**, *115*, 14859–14865.

(16) Lee, C.-Y.; McCammon, J. A.; Rossky, P. J. The Structure of Liquid Water at an Extended Hydrophobic Surface. *J. Chem. Phys.* **1984**, *80*, 4448–4455.

(17) Wallqvist, A.; Berne, B. J. Computer Simulation of Hydrophobic Hydration Forces on Stacked Plates at Short Range. *J. Phys. Chem.* **1995**, *99*, 2893–2899.

(18) Lum, K.; Chandler, D.; Weeks, J. D. Hydrophobicity at Small and Large Length Scales. J. Phys. Chem. B 1999, 103, 4570-4577.

(19) Pratt, L. R.; Chandler, D. Theory of the Hydrophobic Effect. J. Chem. Phys. **1977**, *67*, 3683–3704.

(20) Hummer, G.; Garde, S.; García, A. E.; Pohorille, A.; Pratt, L. R. An Information Theory Model of Hydrophobic Interactions. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 8951–8955.

(21) Vaikuntanathan, S.; Geissler, P. L. Putting Water on a Lattice: The Importance of Long Wavelength Density Fluctuations in Theories

of Hydrophobic and Interfacial Phenomena. *Phys. Rev. Lett.* 2014, 112, No. 020603.

(22) Vaikuntanathan, S.; Rotskoff, G.; Hudson, A.; Geissler, P. L. Necessity of Capillary Modes in a Minimal Model of Nanoscale Hydrophobic Solvation. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*, E2224–E2230.

(23) Wallqvist, A.; Gallicchio, E.; Levy, R. M. A Model for Studying Drying at Hydrophobic Interfaces: Structural and Thermodynamic Properties. *J. Phys. Chem. B* **2001**, *105*, 6745–6753.

(24) 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.

(25) Maibaum, L.; Dinner, A. R.; Chandler, D. Micelle Formation and the Hydrophobic Effect. J. Phys. Chem. B 2004, 108, 6778–6781.

(26) Giovambattista, N.; Lopez, C. F.; Rossky, P. J.; Debenedetti, P. G. Hydrophobicity of Protein Surfaces: Separating Geometry from Chemistry. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 2274–2279.

(27) Giovambattista, N.; Debenedetti, P. G.; Rossky, P. J. Hydration Behavior Under Confinement by Nanoscale Surfaces with Patterned Hydrophobicity and Hydrophilicity. *J. Phys. Chem. C* 2007, *111*, 1323–1332.

(28) Zhang, M.; Nguyen, Q. T.; Ping, Z. Hydrophilic Modification of Poly (Vinylidene Fluoride) Microporous Membrane. *J. Membr. Sci.* **2009**, *327*, 78–86.

(29) Hatakeyama, E. S.; Ju, H.; Gabriel, C. J.; Lohr, J. L.; Bara, J. E.; Noble, R. D.; Freeman, B. D.; Gin, D. L. New Protein-Resistant Coatings for Water Filtration Membranes Based on Quaternary Ammonium and Phosphonium Polymers. *J. Membr. Sci.* **2009**, *330*, 104–116.

(30) Schellenberger, F.; Encinas, N.; Vollmer, D.; Butt, H.-J. How Water Advances on Superhydrophobic Surfaces. *Phys. Rev. Lett.* **2016**, *116*, No. 096101.

(31) de Gennes, P. G. Wetting: Statics and Dynamics. *Rev. Mod. Phys.* **1985**, *57*, 827–863.

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

(33) Joanny, J. F.; de Gennes, P. G. A Model for Contact Angle Hysteresis. J. Chem. Phys. **1984**, 81, 552–562.

(34) Gao, L.; McCarthy, T. J. Contact Angle Hysteresis Explained. Langmuir 2006, 22, 6234-6237.

(35) Law, K.-Y.; Zhao, H. Surface Wetting; Springer International Publishing, 2016; pp 99–121.

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

(37) Cohen-Tanugi, D.; Grossman, J. C. Water Desalination Across Nanoporous Graphene. *Nano Lett.* **2012**, *12*, 3602–3608.

(38) Cohen-Tanugi, D.; Grossman, J. C. Water permeability of Nanoporous Graphene at Realistic Pressures for Reverse Osmosis Desalination. *J. Chem. Phys.* **2014**, *141*, No. 074704.

(39) 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.

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

(41) Zhu, F.; Tajkhorshid, E.; Schulten, K. Collective Diffusion Model for Water Permeation through Microscopic Channels. *Phys. Rev. Lett.* **2004**, 93, No. 224501.

(42) Dashtpour, R.; Al-Zubaidy, S. N. Energy Efficient Reverse Osmosis Desalination Process. *Int. J. Environ. Sci. Develop.* **2012**, *3*, 339.

(43) Zhu, F.; Tajkhorshid, E.; Schulten, K. Pressure-Induced Water Transport in Membrane Channels Studied by Molecular Dynamics. *Biophys. J.* **2002**, *83*, 154–160.

(44) Kannam, S. K.; Todd, B. D.; Hansen, J. S.; Daivis, P. J. Slip Length of Water on Graphene: Limitations of Non-Equilibrium Molecular Dynamics Simulations. *J. Chem. Phys.* **2012**, *136*, No. 024705. (45) Joseph, S.; Aluru, N. R. Why Are Carbon Nanotubes Fast Transporters of Water? *Nano Lett.* **2008**, *8*, 452–458.

(46) Liu, L.; Patey, G. N. Simulated Conduction Rates of Water Through a (6,6) Carbon Nanotube Strongly Depend on Bulk Properties of the Model Employed. *J. Chem. Phys.* **2016**, *144*, No. 184502.

(47) Kalra, A.; Garde, S.; Hummer, G. Osmotic Water Transport Through Carbon Nanotube Membranes. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 10175–10180.

(48) Thomas, J. A.; McGaughey, A. J. H. Reassessing Fast Water Transport Through Carbon Nanotubes. *Nano Lett.* **2008**, *8*, 2788–2793.

(49) Kannam, S. K.; Todd, B. D.; Hansen, J. S.; Daivis, P. J. How Fast Does Water Flow in Carbon Nanotubes? *J. Chem. Phys.* 2013, 138, No. 094701.

(50) Walther, J. H.; Ritos, K.; Cruz-Chu, E. R.; Megaridis, C. M.; Koumoutsakos, P. Barriers to Superfast Water Transport in Carbon Nanotube Membranes. *Nano Lett.* **2013**, *13*, 1910–1914.

(51) Falk, K.; Sedlmeier, F.; Joly, L.; Netz, R. R.; Bocquet, L. Molecular Origin of Fast Water Transport in Carbon Nanotube Membranes: Superlubricity Versus Curvature Dependent Friction. *Nano Lett.* **2010**, *10*, 4067–4073.

(52) Heiranian, M.; Farimani, A. B.; Aluru, N. R. Water Desalination with a Single-Layer MoS₂ Nanopore. *Nat. Commun.* 2015, *6*, No. 8616.
(53) Xue, M.; Qiu, H.; Guo, W. Exceptionally Fast Water

Desalination at Complete Salt Rejection by Pristine Graphyne Monolayers. *Nanotechnology* **2013**, *24*, No. 505720.

(54) Lei, W.; Portehault, D.; Liu, D.; Qin, S.; Chen, Y. Porous Boron Nitride Nanosheets for Effective Water Cleaning. *Nat. Commun.* **2013**, *4*, No. 1777.

(55) Garnier, L.; Szymczyk, A.; Malfreyt, P.; Ghoufi, A. Physics Behind Water Transport Through Nanoporous Boron Nitride and Graphene. J. Phys. Chem. Lett. **2016**, *7*, 3371–3376.

(56) Miró, P.; Audiffred, M.; Heine, T. An Atlas of Two-Dimensional Materials. *Chem. Soc. Rev.* **2014**, *43*, 6537.

(57) Huang, X.; Zhou, R.; Berne, B. J. Drying and Hydrophobic Collapse of Paraffin Plates. J. Phys. Chem. B 2005, 109, 3546–3552.

(58) Zuriguel, I.; Parisi, D. R.; Hidalgo, R. C.; Lozano, C.; Janda, A.; Gago, P. A.; Peralta, J. P.; Ferrer, L. M.; Pugnaloni, L. A.; Clément, E.; et al. Clogging Transition of Many-Particle Systems Flowing Through Bottlenecks. *Sci. Rep.* **2014**, *4*, No. 7324.

(59) Lafond, P. G.; Gilmer, M. W.; Koh, C. A.; Sloan, E. D.; Wu, D. T.; Sum, A. K. Orifice Jamming of Fluid-Driven Granular Flow. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2013**, *87*, No. 042204.

(60) To, K.; Lai, P.-Y.; Pak, H. K. Jamming of Granular Flow in a Two-Dimensional Hopper. *Phys. Rev. Lett.* 2001, *86*, 71-74.

(61) Helbing, D.; Johansson, A.; Mathiesen, J.; Jensen, M. H.; Hansen, A. Analytical Approach to Continuous and Intermittent Bottleneck Flows. *Phys. Rev. Lett.* **2006**, *97*, No. 168001.

(62) Masuda, T.; Nishinari, K.; Schadschneider, A. Critical Bottleneck Size for Jamless Particle Flows in Two Dimensions. *Phys. Rev. Lett.* **2014**, *112*, No. 138701.

(63) Evans, D. J.; Morriss, G. *Statistical Mechanics of Nonequilibrium Liquids*, 2nd ed; Cambridge University Press: Cambridge, 2008.

(64) Evans, D. J.; Hoover, W. G.; Failor, B. H.; Moran, B.; Ladd, A. J. C. Nonequilibrium Molecular Dynamics via Gauss's Principle of Least Constraint. *Phys. Rev. A* **1983**, *28*, 1016–1021.

(65) Frenkel, D.; Smit, B. Understanding Molecular Simulation: From Algorithms to Applications, 2nd ed.; Academic Press: San Diego, 2001.
(66) Evans, D. J.; Morriss, G. P. Non-Newtonian Molecular Dynamics. Comput. Phys. Rep. 1984, 1, 297–343.

(67) Hoover, W. G.; Ladd, A. J. C.; Moran, B. High-Strain-Rate Plastic Flow Studied via Nonequilibrium Molecular Dynamics. *Phys. Rev. Lett.* **1982**, *48*, 1818–1820.

(68) Evans, D. J. Computer "Experiment" for Nonlinear Thermodynamics of Couette Flow. J. Chem. Phys. 1983, 78, 3297–3302.

(69) Evans, D. J.; Morriss, G. P. Shear Thickening and Turbulence in Simple Fluids. *Phys. Rev. Lett.* **1986**, *56*, 2172–2175.

(70) Goldstein, H.; Poole, C. P., Jr.; Safko, J. L. *Classical Mechanics*, 3rd ed.; Pearson: San Francisco, 2001.

(71) Cronström, C.; Raita, T. On Nonholonomic Systems and Variational Principles. J. Math. Phys. 2009, 50, No. 042901.

(72) Flannery, M. R. The Elusive d'Alembert-Lagrange Dynamics of Nonholonomic Systems. *Am. J. Phys.* **2011**, *79*, 932–944.

(73) Edberg, R.; Evans, D. J.; Morriss, G. P. Constrained Molecular Dynamics: Simulations of Liquid Alkanes with a New Algorithm. *J. Chem. Phys.* **1986**, *84*, 6933–6939.

(74) Morriss, G. P.; Evans, D. J. A Constraint Algorithm for the Computer Simulation of Complex Molecular Liquids. *Comput. Phys. Commun.* **1991**, *62*, 267–278.

(75) Nosé, S. A Unified Formulation of the Constant Temperature Molecular Dynamics Methods. J. Chem. Phys. **1984**, 81, 511–519.

(76) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A* 1985, 31, 1695–1697.

(77) Huang, C.; Nandakumar, K.; Choi, P. Y. K.; Kostiuk, L. W. Molecular Dynamics Simulation of a Pressure-Driven Liquid Transport Process in a Cylindrical Nanopore Using Two Self-Adjusting Plates. *J. Chem. Phys.* **2006**, *124*, No. 234701.

(78) Huang, C.; Choi, P. Y. K.; Kostiuk, L. W. A Method for Creating a Non-Equilibrium $NT(P_1-P_2)$ Ensemble in Molecular Dynamics Simulation. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20750.

(79) Müller-Plathe, F. A Simple Nonequilibrium Molecular Dynamics Method for Calculating the Thermal Conductivity. *J. Chem. Phys.* **1997**, *106*, 6082–6085.

(80) Frentrup, H.; Avendaño, C.; Horsch, M.; Salih, A.; Müller, E. A. Transport Diffusivities of Fluids in Nanopores by Non-Equilibrium Molecular Dynamics Simulation. *Mol. Simul.* **2012**, *38*, 540–553.

(81) Takaba, H.; Onumata, Y.; Nakao, S.-I. Molecular Simulation of Pressure-Driven Fluid Flow in Nanoporous Membranes. *J. Chem. Phys.* **2007**, *127*, No. 054703.

(82) Ying-Hua, Q.; Kun, L.; Wei-Yu, C.; Wei, S.; Qi-Yan, T.; Yun-Fei, C. Ion and Water Transport in Charge-Modified Graphene Nanopores. *Chin. Phys. B* 2015, 24, No. 108201.

(83) Weeks, J. D.; Chandler, D.; Andersen, H. C. Role of Repulsive Forces in Determining the Equilibrium Structure of Simple Liquids. *J. Chem. Phys.* **1971**, *54*, 5237–5247.

(84) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. The Missing Term in Effective Pair Potentials. *J. Phys. Chem.* **1987**, *91*, 6269–6271.

(85) Ryckaert, J.-P.; Ciccotti, G.; Berendsen, H. J. C. Numerical Integration of the Cartesian Equations of Motion of a System with Constraints: Molecular Dynamics of n-Alkanes. *J. Comput. Phys.* **1977**, 23, 327–341.

(86) 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.

(87) Hockney, R. W.; Eastwood, J. W. Computer Simulation Using Particles; Taylor & Francis: New York, 1989.

(88) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. J. Comput. Phys. **1995**, 117, 1–19.

(89) Humphrey, W.; Dalke, A.; Schulten, K. VMD–Visual Molecular Dynamics. J. Mol. Graphics **1996**, *14*, 33–38.

(90) Stone, J. An Efficient Library for Parallel Ray Tracing and Animation. Ph.D. Thesis, Computer Science Department, University of Missouri-Rolla, 1998.

(91) Irving, J. H.; Kirkwood, J. G. The Statistical Mechanical Theory of Transport Processes. IV. The Equations of Hydrodynamics. *J. Chem. Phys.* **1950**, *18*, 817–829.

(92) Todd, B. D.; Evans, D. J.; Daivis, P. J. Pressure Tensor for Inhomogeneous Fluids. *Phys. Rev. E* **1995**, *52*, 1627–1638.

(93) Hafskjold, B.; Ikeshoji, T. Microscopic Pressure Tensor for Hard-Sphere Fluids. *Phys. Rev. E* 2002, *66*, No. 011203.

(94) Heinz, H. Calculation of Local and Average Pressure Tensors in Molecular Simulations. *Mol. Simul.* **2007**, *33*, 747–758.

(95) Zimmerman, J. A.; Webb, E. B., III; Hoyt, J. J.; Jones, R. E.; Klein, P. A.; Bammann, D. J. Calculation of Stress in Atomistic Simulation. *Modell. Simul. Mater. Sci. Eng.* **2004**, *12*, S319. (96) Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. Nanoscale Hydrodynamics: Enhanced Flow in Carbon Nanotubes. *Nature* **2005**, 438, 44.

(97) Holt, J. K.; Park, H. G.; Wang, Y.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. Fast Mass Transport Through Sub-2-Nanometer Carbon Nanotubes. *Science* **2006**, *312*, 1034–1037.

(98) Whitby, M.; Cagnon, L.; Thanou, M.; Quirke, N. Enhanced Fluid Flow through Nanoscale Carbon Pipes. *Nano Lett.* **2008**, *8*, 2632–2637.

(99) Sinha, S.; Rossi, M. P.; Mattia, D.; Gogotsi, Y.; Bau, H. H. Induction and Measurement of Minute Flow Rates Through Nanopipes. *Phys. Fluids* **2007**, *19*, No. 013603.

(100) Koplik, J.; Banavar, J. R.; Willemsen, J. F. Molecular Dynamics of Fluid Flow at Solid Surfaces. *Phys. Fluids A.* **1989**, *1*, 781–794.

(101) Galea, T. M.; Attard, P. Molecular Dynamics Study of the Effect of Atomic Roughness on the Slip Length at the Fluid-Solid Boundary During Shear Flow. *Langmuir* **2004**, *20*, 3477–3482.

(102) Barrat, J.-L.; Bocquet, L. Large Slip Effect at a Nonwetting Fluid-Solid Interface. *Phys. Rev. Lett.* **1999**, *82*, 4671–4674.

(103) Cottin-Bizonne, C.; Barentin, C.; Charlaix, É; Bocquet, L.; Barrat, J.-L. Dynamics of Simple Liquids at Heterogeneous Surfaces: Molecular-Dynamics Simulations and Hydrodynamic Description. *Eur. Phys. J. E: Soft Matter Biol. Phys.* **2004**, *15*, 427–438.

(104) Sokhan, V. P.; Nicholson, D.; Quirke, N. Fluid Flow in Nanopores: Accurate Boundary Conditions for Carbon Nanotubes. J. Chem. Phys. 2002, 117, 8531–8539.

(105) Thomas, M.; Corry, B. Thermostat Choice Significantly Influences Water Flow Rates in Molecular Dynamics Studies of Carbon Nanotubes. *Microfluid. Nanofluid.* **2015**, *18*, 41–47.

(106) Alder, B. J.; Wainwright, T. E. Velocity Autocorrelations for Hard Spheres. *Phys. Rev. Lett.* **1967**, *18*, 988–990.

(107) Alder, B. J.; Wainwright, T. E. Decay of the Velocity Autocorrelation Function. *Phys. Rev. A* **1970**, *1*, 18–21.

(108) Pomeau, Y.; Resibois, P. Time Dependent Correlation Functions and Mode-Mode Coupling Theories. *Phys. Rep.* **1975**, *19*, 63–139.

(109) Thompson, P. A.; Troian, S. M. A General Boundary Condition for Liquid Flow at Solid Surfaces. *Nature* **1997**, *389*, 360–362.

(110) Ostrowski, J. H. J.; Eaves, J. D. The Tunable Hydrophobic Effect on Electrically Doped Graphene. J. Phys. Chem. B 2014, 118, 530–536.

(111) Hong, G.; Han, Y.; Schutzius, T. M.; Wang, Y.; Pan, Y.; Hu, M.; Jie, J.; Sharma, C. S.; Müller, U.; Poulikakos, D. On the Mechanism of Hydrophilicity of Graphene. *Nano Lett.* **2016**, *16*, 4447–4453.

(112) Ashraf, A.; Wu, Y.; Wang, M. C.; Yong, K.; Sun, T.; Jing, Y.; Haasch, R. T.; Aluru, N. R.; Nam, S. Doping-Induced Tunable Wettability and Adhesion of Graphene. *Nano Lett.* **2016**, *16*, 4708–4712.

(113) Farmer, D. B.; Golizadeh-Mojarad, R.; Perebeinos, V.; Lin, Y.-M.; Tulevski, G. S.; Tsang, J. C.; Avouris, P. Chemical Doping and Electron-Hole Conduction Asymmetry in Graphene Devices. *Nano Lett.* **2009**, *9*, 388–392.

(114) Bao, W.; Myhro, K.; Zhao, Z.; Chen, Z.; Jang, W.; Jing, L.; Miao, F.; Zhang, H.; Dames, C.; Lau, C. N. In Situ Observation of Electrostatic and Thermal Manipulation of Suspended Graphene Membranes. *Nano Lett.* **2012**, *12*, 5470–5474.

(115) Liu, H.; Liu, Y.; Zhu, D. Chemical Doping of Graphene. J. Mater. Chem. 2011, 21, 3335–3345.

(116) Panchakarla, L. S.; Subrahmanyam, K. S.; Saha, S. K.; Govindaraj, A.; Krishnamurthy, H. R.; Waghmare, U. V.; Rao, C. N. R. Synthesis, Structure, and Properties of Boron- and Nitrogen-Doped Graphene. *Adv. Mater.* **2009**, *21*, 4726–4730.

(117) Willard, A. P.; Chandler, D. The Molecular Structure of the Interface Between Water and a Hydrophobic Substrate is Liquid-Vapor Like. *J. Chem. Phys.* **2014**, *141*, No. 18C519.

(118) Clauset, A.; Shalizi, C.; Newman, M. Power-Law Distributions in Empirical Data. *SIAM Rev.* **2009**, *51*, 661–703.

(119) Zuriguel, I.; Pugnaloni, L. A.; Garcimartín, A.; Maza, D. Jamming During the Discharge of Grains from a Silo Described as a Percolating Transition. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2003**, *68*, No. 030301.

(120) Saloma, C.; Perez, G. J.; Tapang, G.; Lim, M.; Palmes-Saloma, C. Self-Organized Queuing and Scale-Free Behavior in Real Escape Panic. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 11947–11952.

(121) Metzler, R.; Klafter, J. The Random Walk's Guide to Anomalous Diffusion: A Fractional Dynamics Approach. *Phys. Rep.* **2000**, 339, 1–77.

(122) Hansen, J.-P.; Verlet, L. Phase Transitions of the Lennard-Jones System. *Phys. Rev.* **1969**, *184*, 151–161.

(123) Rowley, R. L.; Painter, M. M. Diffusion and Viscosity Equations of State for a Lennard-Jones Fluid Obtained from Molecular Dynamics Simulations. *Int. J. Thermophys.* **1997**, *18*, 1109–1121.