RAPID COMMUNICATION | SEPTEMBER 03 2024

The entropic origin of the enhancement of liquid diffusion close to a neutral confining surface

Special Collection: 2024 JCP Emerging Investigators Special Collection

Lorenzo Agosta ; Wim Briels ; Kersti Hermansson ; Mikhail Dzugutov

J. Chem. Phys. 161, 091102 (2024)
https://doi.org/10.1063/5.0224016

The Journal of Chemical Physics COMMUNICATION pubs.aip.org/aip/jcp

The entropic origin of the enhancement of liquid diffusion close to a neutral confining surface

Cite as: J. Chem. Phys. 161, 091102 (2024); doi: 10.1063/5.0224016
Submitted: 18 June 2024 • Accepted: 13 August 2024 •
Published Online: 3 September 2024

Lorenzo Agosta,[1,2,a)] Wim Briels,[3,4] Kersti Hermansson,[2] and Mikhail Dzugutov[2]

AFFILIATIONS

[1] Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA
[2] Uppsala University, Ångström Laboratory, Department of Chemistry, 75121 Uppsala, Sweden
[3] University of Twente, Computational Chemical Physics, Postbus 217, Enschede 7500AE, Netherlands
[4] IBI-4:Biomacromolecular Systems and Processes, Forschungszentrum Jülich GmbH, Juelich D-52428, Germany

Note: This paper is part of the 2024 JCP Emerging Investigators Special Collection.
[a)] **Author to whom correspondence should be addressed:** la5399@princeton.edu

ABSTRACT

It is known that, in the proximity of a neutral wall, liquids experience diffusion enhancement relative to their bulk diffusion, but the origin of this phenomenon is still unknown. We report a molecular dynamics simulation investigating the dynamics of a simple liquid in the proximity to a non-interacting smooth confining wall, which exhibits a strong diffusion enhancement within the liquid layers adjacent to the wall. We present an analysis of these results, demonstrating that the observed diffusion enhancement can be accounted for, with numerical accuracy, using the universal scaling law that relates the liquid diffusion rate to the excess entropy. These results show that the scaling law, which has so far only been used for the description of the bulk liquid diffusion, can be successfully used to describe the diffusion in liquids under nano-scale confinement.

Diffusion is a fundamental and the most ubiquitous property of the liquid state, but its many aspects still elude a comprehensive understanding on the microscopic level. The statistical theory is still unable to predict the rate of diffusion in a liquid based on the information on the inter-particle interaction forces. One of the intriguing phenomena posing a problem for the liquid theory is the enhancement of the diffusion in the proximity of a non-interactive confining surface that was observed in many liquids of widely different nature, from water to liquid noble gases.[1–5]

Structural and dynamical properties of liquids confined in nanometer-sized channels or pores are known to be different from those of the respective bulk liquids.[6–8] In recent years, considerable research efforts have been focused on investigating the changes of the properties of water upon nanoscale confinement.[9–11] Understanding these changes is of significant interest for a wide range of applications, e.g., biological systems,[12–14] flow of organic compounds into inorganic media,[15] the diffusion properties of materials, such as zeolites[16] and clay,[17] water diffusion in nanotubes,[18,19] and photovoltaic materials as perovskites.[20,21] In all these cases is key to address the liquid properties' changes with respect to the properties of the confining materials. A fundamental question is whether the dynamical properties of confined water can be regarded as independent of confining surfaces or if confinement always has a dominant influence on the nanoscale liquid. It is established both in real experiments and in atomistic simulations that the hydrophilic confining surfaces significantly slow down the dynamics of confined water within several adjacent layers.[7,10,11,22–26] On the other hand, it was found that the proximity of a hydrophobic confining surface results in an observable enhancement of the diffusion and other dynamical properties of water.[1–3,7,11,17,18,26–29]

Similar effects of enhanced dynamics under nanoscopic-scale confinement were also observed in a wide range of other liquids, from polymers[30] to simple atomic systems,[4,7,31] which indicates the universal nature of this phenomenon. So far, no comprehensive unifying explanation of these puzzling observations has been proposed. In the case of water, it was suggested[3,32] that the enhanced molecular mobility can be a result of the reduction of the number of the hydrogen bonds due to the presence of a neutral hydrophobic surface. This conjecture, however, cannot explain the fact that a similar enhancement effect was observed in liquids composed of

particles with spherically symmetric interactions near the smooth neutral or repulsive surface.[4,11,26] Hence, a more general mechanism is needed to explain the universality of the observed enhancement. The most general mechanism that can be conceived is based on purely geometric considerations.

In this paper, we suggest such a mechanism. In order to resemble the condition of an hydrophobic wall,[2] discarding the influence of attracting forces and surface roughness,[4] we consider the ideal case of a molecular dynamics simulation of a simple liquid under confinement by a smooth neutral wall. We observe a significant enhancement of the lateral diffusion in the layers adjacent to the wall. Evidence is presented that the observed diffusion enhancement near the neutral smooth repulsive wall is of purely entropic origin. We demonstrate that the enhancement effect can be quantitatively accounted by using an earlier reported scaling law for liquid diffusion[33,34] that relates the diffusion rate to the local excess entropy. The results of this study also show that this law that has earlier only been tested for its description of diffusion in bulk liquids can be successfully applied to the description of the diffusion in liquids under nanoscale confinement.

We start with recalling the fundamental connection between the dynamical properties of dense liquids and their liquid structure. The structural relaxation and transport properties of dense liquids are dominated by a mechanism called "cage diffusion." This term was coined by Cohen[35] who recognized the corresponding mechanism in connection with a specific feature of the neutron scattering spectra of simple dense liquids, the so-called de Gennes narrowing,[36] which refers to the reduction of the half-width of the spectra around the wave vector Q_0 corresponding to the position of the main peak of the structure factor $S(Q)$.[37] This wavelength manifests the dominant periodicity of the local order in dense liquids with a period corresponding to the average nearest-neighbor distance in the liquid. This structure can be viewed as a local order generated by the cage of nearest neighbors in which each particle remains confined for a measurable time. The elementary diffusive motion of a particle can only be possible as a result of rearrangements of its cage. In this way, the diffusion dynamics in dense liquids is fundamentally coupled with the local structural relaxation dynamics. On the other hand, the effect of de Gennes narrowing demonstrates that the relaxation dynamics is controlled by the liquid structure manifested by the main peak of structure factor $S(Q)$, the latter being the Fourier-transform of the density radial distribution function $g(r)$.[37]

The proximity of a confining surface significantly reduces the number of neighbors involved in the local structural environment of a liquid particle. As concluded above it, this is also expected to affect the liquid structural relaxation and, thereby, the diffusion rate. Now, we have the following problem. The liquid structure is expressed by either the structure factor or the radial distribution function. On the other hand, the diffusion coefficient is a number. In order to construct a theoretical model connecting the self-diffusion coefficient in a liquid to its structure, we have to quantify the latter with a single quantity. In general, the structure of a liquid is a full set of correlation functions describing the mutual arrangement of its particles. We therefore need to use a functional of these correlation functions that would be possible to relate to the diffusion coefficient. This functional is the excess entropy $S_{ex} = S - S_{pg}$, where S is the system's total entropy and S_{pg} is the entropy of the perfect gas.[38–41]

The process of structural relaxation in a liquid can be viewed as a random walk in the 3N-dimensional space of its configurations where N is the number of particles. It is assumed that an elementary step in this process is a local particle rearrangement moving the system to a new configuration point. It only happens if the destination configuration is open, the probability of which can be expressed through the excess entropy as $e^{S_{ex}}$. Therefore, the diffusion coefficient might be considered to scale universally as[33,34]

$$D = D_0 e^{s_{ex}}, \tag{1}$$

where lower case s refers to the entropy per particle. The excess entropy can be expanded in terms of the contributions from n-body correlation functions as

$$s_{ex} = s - s_{pg} = \sum_{n=2} s_n. \tag{2}$$

We note that the kinetic theories of liquid state are essentially two-body theories, usually based on the hard-sphere model approximation.[35] Therefore, we assume that, for the present application, the excess entropy in Eq. (2) can be restricted to the two-body approximation. For an isotropic liquid environment, the two-body correlation function can be reduced to the spherically symmetric radial distribution function $g(r)$,[37] and the respective two-body excess entropy approximation can be expressed as[38–41]

$$s_2 = -2\pi\rho \int_0^\infty \{g(r)\ln[g(r)] - [g(r)-1]\} r^2 dr. \tag{3}$$

With this form of the excess entropy using the time scale in terms of the hard-sphere collision frequency and the length scale in terms of the hard-sphere diameter, both obtained from $g(r)$, Eq. (1) can universally relate the liquid diffusion coefficient to the liquid structure.[33,34] This universal scaling law was found to be successful in describing diffusion in a wide variety of liquids,[42–44] as well as in the solid ionic conductor AgI.[33] Using the same approach, a universal relation between thermodynamic entropy and Kolmogorov–Sinai entropy was found.[45] We note that for more complex molecular liquids, such as water, a more accurate estimate of s_{ex} might be needed. Here, we will use Eq. (1) to analyze the phenomenon of the dynamics enhancement in simple liquid near a confining surface.

First, we have to estimate how the local excess entropy s_2 is modified by the proximity of the non-interactive confining surface. For that purpose, we have to modify Eq. (3) in order to take into account the loss of correlations truncated by the wall. The area of the segment of a sphere of radius r truncated by a plane at the distance d from its center is

$$A = 2\pi r(r+d). \tag{4}$$

Accordingly, the part of s_2 that represents the correlations of the central particle with the particles that happened to be within the segment of the sphere cut by the wall can be estimated as

$$s_2(d) = -\pi\rho \int_d^\infty \{g(r)\ln[g(r)] - [g(r)-1]\} r(r+d) dr - 2\pi\rho \int_0^d \{g(r)\ln[g(r)] - [g(r)-1]\} r^2 dr, \tag{5}$$

where $g(r)$ is the radial distribution function calculated for the liquid bulk. A schematic illustration of this formulation is present in the supplementary material. The entropy gain can then be evaluated as

$$\Delta s_2(d) = s_2(d) - s_2. \tag{6}$$

According to the scaling law (1), this gain of entropy due to the loss of correlation beyond the confining wall is expected to result in an enhancement of the diffusion rate for the particles near the wall, which can be estimated as

$$D(d)/D_{bulk} = e^{\Delta s_2(d)}, \tag{7}$$

where D and D_{bulk} are the diffusion rates at the distance d from the wall and in the bulk liquid, respectively.

In order to test this conjecture, we performed molecular-dynamics (MD) simulations of a dense liquid consisting of 17 820 particles interacting via the Lennard-Jones (LJ) pair potential. The simulations were carried out at density $\rho = 0.93$ and two different temperatures $T_1 = 0.91$ and $T_2 = 0.66$ (close to the LJ triple point), for which Eq. (1) was demonstrated to hold.[33] All the quantities we report are expressed in the LJ reduced units. The system was confined to a cubic box where the boundary conditions were assumed to be periodic in two dimensions (X and Y) and confined between two walls perpendicular to the Z axis. The interaction between the constituent particles and the wall at the distance d was described by the potential energy function $U(r) = k(r - d_0)^b$, where $d_0 = 0.5$ is the position of the wall, $k = 10^9$ is the force constant, and $b = 4$ relates to the stiffness of the wall. The GROMACS[46] software was used for the MD simulations in combination with PLUMED[44] for the wall constraints.

In Fig. 1, we show the variation of the liquid density along the direction perpendicular to the wall. The density profile was calculated for the two temperatures that we explored in this simulation. One can see that the proximity of the wall induces a layered structure, which persists up to seven particle unit from the wall, as usual for liquid close to rigid interfaces.[6,48] As can be expected, the results also show that the effect of the wall on the structure is stronger at higher temperature. We note that the first peak in the density profile corresponds to the average position of the particles closest to the wall.

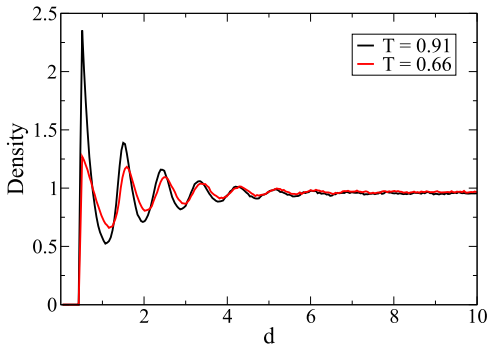

FIG. 1. The density profiles along the direction perpendicular to the wall for the confined LJ liquid at the two simulated temperatures.

The observed effect of the fluctuations of the liquid density in the proximity of the wall implies that corrections need to be introduced to Eq. (5). Moreover, the density change might induce rearrangements of the liquid local structure, which implies at least a dependence of $g(r)$ on the distance from the wall. As a first approximation, we will still consider $g(r)$ isotropic, discarding its angular coordination. In order to take into account the effect of liquid structure fluctuations induced by the proximity of the wall upon the excess entropy, we modify Eq. (5) as follows:

$$\begin{aligned} s_2^{corr}(d) = &-\pi\rho(d)\int_d^\infty \{g(r,d)\ln[g(r,d)] \\ &- [g(r,d)-1]\}r(r+d)dr \\ &- 2\pi\rho(d)\int_0^d \{g(r,d)\ln[g(r,d)] \\ &- [g(r,d)-1]\}r^2 dr. \end{aligned} \tag{8}$$

Here, $\rho(d)$ and $g(r,d)$ are calculated as functions of d by considering a layer of one particle diameter thickness, which is sequentially shifted by 0.143 unit length along the z direction. The d values are taken as the layer center. When $r < d$, $g(r,d)$ is calculated as usually as $\frac{n(r,d)}{4\pi r^2\rho\Delta r}$, where ρ is the density of the system and $n(r,d)$ are the mean number of particles in a shell of width Δr at distance r. Here, the distance r is taken only between the particles within the considered layer (centered in d) and the rest of the system. When $r > d$, $g(r,d)$ is calculated as $\frac{n(r,d)}{A\rho\Delta r}$, where A is the area of the cross section defined by Eq. (4). We note that the position of the truncation plane is assumed to be defined by the average particle position next to the wall rather than that of the wall.

Accordingly, we use this corrected expression for the pair excess entropy near the truncating wall to modify Eq. (6) to produce a corrected expression for the entropy gain,

$$\Delta s_2^{corr}(d) = s_2^{corr}(d) - s_2. \tag{9}$$

Accordingly, Eq. (7) becomes

$$D(d)/D_{bulk} = e^{\Delta s_2^{corr}(d)}. \tag{10}$$

In order to investigate the effect of the entropy variation, induced by the confining wall, on the liquid diffusion, we computed the lateral diffusion in planes perpendicular to the wall. When an anisotropic external potential is acting on the system, like a rigid wall, the translational diffusion constant is determined from the Smoluchowski equation.[24,49] The components of the diffusion coefficient parallel to the wall are evaluated from the mean-square displacement (MSD) corrected by the probability for a particle to stay within the layer during the time interval t,

$$D_{xy}(d) = \frac{1}{4}\lim_{t\to\infty}\frac{\mathrm{MSD}_{xy}(d,t)}{tP(d,t)}, \tag{11}$$

where the MSD is defined in a layer at the distance d from the wall. $P(d,t)$ is the probability that a particle stays in the layer within time interval t.[25] In all layers, the latter time was found to be sufficient for

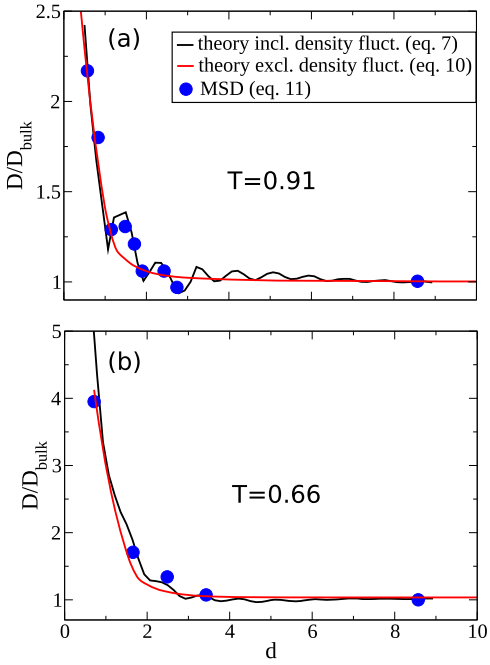

FIG. 2. Diffusion rate enhancement at the distance d from the confining wall (relative to the bulk value) calculated for the two indicated temperatures. Dots, diffusion coefficient values in the layers of simulated liquid calculated in molecular dynamics (MD) at the indicated distance from the confining wall according to Eq. (11). The dots positions are defined as the center of the respective layer thickness (0.3 or 0.6 LJ units). The curves indicate the diffusion coefficient as a function of the distance from the wall calculated according to the entropy scaling law, Eqs. (7) and (10), using either Eq. (5) or Eq. (8), respectively.

the particles to exhibit a long enough linear regime of MSD needed for the reliable calculation of the diffusion coefficient.

In Fig. 2, we present the results of the described calculations of the in-layer lateral diffusion rate as a function of the layer's distance from the wall. The results demonstrate a pronounced diffusion enhancement apparently induced by the proximity of the confining wall. Notably, the enhancement effect increases from factor 2 to 4 in the first layer as the liquid temperature decreases from $T = 0.91$ to $T = 0.66$. This is in good agreement with the similar results obtained in simulations and experiments of water close to hydrophobic surfaces. An enhancement factor up to three was observed for water–graphene interfaces,[1] a factor up to two was calculated for water–ceria interfaces,[2] and a factor up to 20% was reported for water confined in some clay structures.[17] The observed enhancement effect is confined to the distance of several layers from the wall.

The measured diffusion data presented in Fig. 2 are compared with the expected diffusion enhancement as predicted by the model we presented above based on the entropy scaling law for liquid diffusion, Eqs. (4)–(10). The agreement is very good, particularly for the case of entropy calculation, which took into account the local density fluctuations at the wall (reflecting the respective behavior of the density profile, Fig. 1). The increase of the enhancement effect at a lower temperature is consistent with the respective increase of the entropy gain Δs_2 (as visible in Fig. S1 in the supplementary material) apparently caused by stronger structural correlations. In addition, we note better agreement between the diffusion measured with Eqs. (7) and (11) at low temperature, where the density oscillation is much smoother. This confirms that the structural modulations imposed by the wall play a minor role in assessing the enhancement of the diffusion.

The error in the theoretical prediction of the diffusion enhancement according to the entropy scaling relation arises from the reduction of the full excess entropy s_{ex} to its two-body approximation s_2. Using the results reported in Ref. 38, the estimated share of contributions to the excess entropy beyond the two-body approximation in the LJ liquid around its triple point is about 7%. We mention an alternative relation between liquid diffusion and excess entropy[50] where the diffusion rate scales as $e^{\alpha s_{ex}}$, α being a fitting parameter. It is clear that if $\alpha \neq 1$, this scaling law will not reproduce the diffusion enhancement results shown in Fig. 2.[51]

Finally, we note that the simple model described in Eq. (6), which assumes only the knowledge of $g(r)$, provides a quite accurate approximation of the diffusion enhancement (red line in Fig. 2). This implies that the change of $g(r)$ when approaching the wall is rather small and that $g(r, d)$ is a sufficient approximation for describing the entropy variation. This is also important as Eq. (6) can be readily used, in combination with experimental radial distribution functions, for the study of liquid in constrained geometries.

Some concluding remarks are in order.

1. The theoretical model interpreting the diffusion enhancement in liquids near confining walls in terms of the excess entropy scaling law can be easily extended to explain similar diffusion anomalies in liquids near other kinds of surfaces, including the surface separation of coexisting liquid and gas phases. The success of this scaling law in describing diffusion in bulk super-ionic conductors that we mentioned above indicates that it can be possibly used to analyze similar dynamic anomalies of these systems under confinement.
2. It is quite clear from the geometrical arguments that were presented above that the diffusion enhancement effect in liquids induced by the proximity of a confining surface is expected to be stronger if the surface shape is convex with the curvature radius of nanometer scale. This conjecture is of significance for the applications such as water dynamics in nanoporous materials.[19]
3. The presence of surface roughness or weak adhesive surface forces will affect the liquid structure at the interface. The influence of these effects on the liquid interfacial entropy must be carefully checked. This extends to molecular liquids where the estimate of the excess entropy from the two-body approximation might not result sufficient.
4. The results presented here can be regarded as another successful test of the scaling law relating liquid diffusion to the excess entropy. The results demonstrate that the application scope of this law can be extended to include the description of the liquid diffusion in confined geometries. The results of this study thus confirm the universal nature of this law relating the liquid dynamics to the structure. We also note that the result of this study might be of relevance for the behavior of a thin layer of lubricating liquid between solid surfaces.[52]

In summary, we performed a molecular dynamics simulation investigating the effect of confinement on the diffusion in the Lennard-Jones liquid. It is found that the proximity of the confining wall induces a significant diffusion enhancement. We demonstrate that this effect can be successfully accounted for on a quantitative level using the earlier published universal entropy scaling law for the liquid diffusion. The observed diffusion enhancement is shown to be a result of the reduction of (the absolute value of) the local excess entropy, which is caused by the reduction of the structural correlations of a diffusing particle by the confinement. A conceptually significant conclusion of these results is that the application scope of the scaling law we tested here can be extended to the description of the liquid diffusion in constrained geometries.

The supplementary material contains the plot of the excess entropy as a function of the distance from the confining wall calculated using Eqs. (6) and (9) for the two indicated temperatures; a schematic illustration of the excess entropy calculation using Eq. (5).

This work was supported by the Swedish Research Council (VR). We also acknowledge financial support from the Swedish National Strategic e-Science program eSSENCE. The calculations described in this paper were performed using resources provided by the Swedish National Infrastructure for Computing (SNIC) at PDC.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Lorenzo Agosta: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Writing – original draft (equal); Writing – review & editing (equal). **Wim Briels**: Methodology (equal); Supervision (equal); Writing – review & editing (equal). **Kersti Hermansson**: Data curation (equal); Funding acquisition (equal); Supervision (equal); Validation (equal); Writing – review & editing (equal). **Mikhail Dzugutov**: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Supervision (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES

[1]G. Cicero, J. C. Grossman, E. Schwegler, F. Gygi, and G. Galli, "Water confined in nanotubes and between graphene sheets: A first principle study," J. Am. Chem. Soc. **130**, 1871–1878 (2008).

[2]L. Agosta, D. Arismendi-Arrieta, M. Dzugutov, and K. Hermansson, "Origin of the hydrophobic behaviour of hydrophilic CeO_2," Angew. Chem., Int. Ed. **62**, e202303910 (2023).

[3]P. Kumar, S. V. Buldyrev, F. W. Starr, N. Giovambattista, and H. E. Stanley, "Thermodynamics, structure, and dynamics of water confined between hydrophobic plates," Phys. Rev. E **72**, 051503 (2005).

[4]P. Scheidler, W. Kob, and K. Binder, "Cooperative motion and growing length scales in supercooled confined liquids," Europhys. Lett. **59**, 701 (2002).

[5]M. F. Harrach and B. Drossel, "Structure and dynamics of TIP3P, TIP4P, and TIP5P water near smooth and atomistic walls of different hydroaffinity," J. Chem. Phys. **140**, 174501 (2014).

[6]O. Björneholm, M. H. Hansen, A. Hodgson, L.-M. Liu, D. T. Limmer, A. Michaelides, P. Pedevilla, J. Rossmeisl, H. Shen, G. Tocci, E. Tyrode, M.-M. Walz, J. Werner, and H. Bluhm, "Water at interfaces," Chem. Rev. **116**, 7698–7726 (2016).

[7]I. N. Tsimpanogiannis, O. A. Moultos, L. F. M. Franco, M. B. d. M. Spera, M. Erdős, and I. G. Economou, "Self-diffusion coefficient of bulk and confined water: A critical review of classical molecular simulation studies," Mol. Simul. **45**, 425–453 (2019).

[8]L. Agosta, A. Metere, P. Oleynikov, and M. Dzugutov, "Self-assembly of a triply periodic continuous mesophase with Fddd symmetry in simple one-component liquids," J. Chem. Phys. **152**, 191101 (2020).

[9]E. Barry *et al.*, "Advanced materials for energy-water systems: The central role of water/solid interfaces in adsorption, reactivity, and transport," Chem. Rev. **121**, 9450–9501 (2021).

[10]G. J. Wang and N. G. Hadjiconstantinou, "Layered fluid structure and anomalous diffusion under nanoconfinement," Langmuir **34**, 6976–6982 (2018).

[11]F. Leoni and G. Franzese, "Structural behavior and dynamics of an anomalous fluid between attractive and repulsive walls: Templating, molding, and superdiffusion," J. Chem. Phys. **141**, 174501 (2014).

[12]M. J. Limo, A. Sola-Rabada, E. Boix, V. Thota, Z. C. Westcott, V. Puddu, and C. C. Perry, "Interactions between metal oxides and biomolecules: From fundamental understanding to applications," Chem. Rev. **118**, 11118–11193 (2018).

[13]D. Horinek, A. Serr, M. Geisler, T. Pirzer, U. Slotta, S. Q. Lud, J. A. Garrido, T. Scheibel, T. Hugel, and R. R. Netz, "Peptide adsorption on a hydrophobic surface results from an interplay of solvation, surface, and intrapeptide forces," Proc. Natl. Acad. Sci. U. S. A. **105**, 2842–2847 (2008).

[14]M. Rabe, D. Verdes, and S. Seeger, "Understanding protein adsorption phenomena at solid surfaces," Adv. Colloid Interface Sci. **162**, 87–106 (2011).

[15]F. Ruggeri and M. Krishnan, "Entropic trapping of a singly charged molecule in solution," Nano Lett. **18**, 3773–3779 (2018).

[16]C. Parravano, J. D. Baldeschwieler, and M. Boudart, "Diffusion of water in zeolites," Science **155**, 1535–1536 (1967).

[17]F. González Sánchez, F. Jurányi, T. Gimmi, L. Van Loon, T. Unruh, and L. W. Diamond, "Translational diffusion of water and its dependence on temperature in charged and uncharged clays: A neutron scattering study," J. Chem. Phys. **129**, 174706 (2008).

[18]B. H. S. Mendonça, E. E. de Moraes, R. J. C. Batista, A. B. de Oliveira, M. C. Barbosa, and H. Chacham, "Water diffusion in carbon nanotubes for rigid and flexible models," J. Phys. Chem. C **127**, 9769–9778 (2023).

[19]S. Brandani *et al.*, "Diffusion anomaly in nanopores as a rich field for theorists and a challenge for experimentalists," Nat. Commun. **15**, 5721 (2024).

[20]F. H. Isikgor, A. S. Subbiah, M. K. Eswaran, C. T. Howells, A. Babayigit, M. De Bastiani, E. Yengel, J. Liu, F. Furlan, G. T. Harrison, S. Zhumagali, J. I. Khan, F. Laquai, T. D. Anthopoulos, I. McCulloch, U. Schwingenschlögl, and S. De Wolf, "Scaling-up perovskite solar cells on hydrophobic surfaces," Nano Energy **81**, 105633 (2021).

[21]J. Jeong, T. Chawanpunyawat, M. Kim *et al.*, "Carbazole treated waterproof perovskite films with improved solar cell performance," Adv. Energy Mater. (online, 2024).

[22]S. Romero-Vargas Castrillón, N. Giovambattista, I. A. Aksay, and P. G. Debenedetti, "Effect of surface polarity on the structure and dynamics of water in nanoscale confinement," J. Phys. Chem. B **113**, 1438–1446 (2009).

[23]S. Romero-Vargas Castrillón, N. Giovambattista, I. A. Aksay, and P. G. Debenedetti, "Evolution from surface-influenced to bulk-like dynamics in nanoscopically confined water," J. Phys. Chem. B **113**, 7973–7976 (2009).

[24]L. Agosta, E. G. Brandt, and A. P. Lyubartsev, "Diffusion and reaction pathways of water near fully hydrated TiO_2 surfaces from ab initio molecular dynamics," J. Chem. Phys. **147**, 024704 (2017).
[25]L. Agosta, M. Dzugutov, and K. Hermansson, "Supercooled liquid-like dynamics in water near a fully hydrated titania surface: Decoupling of rotational and translational diffusion," J. Chem. Phys. **154**, 094708 (2021).
[26]J. I. Monroe and M. Scott Shell, "Computational discovery of chemically patterned surfaces that effect unique hydration water dynamics," Proc. Natl. Acad. Sci. U. S. A. **115**(32), 8093–8098 (2018).
[27]A. Kayal and A. Chandra, "Orientational order and dynamics of interfacial water near a hexagonal boron-nitride sheet: An ab initio molecular dynamics study," J. Chem. Phys. **147**, 164704 (2017).
[28]M. Chiricotto, F. Martelli, G. Giunta, and P. Carbone, "Role of long-range electrostatic interactions and local topology of the hydrogen bond network in the wettability of fully and partially wetted single and multilayer graphene," J. Phys. Chem. C **125**, 6367–6377 (2021).
[29]S. H. Lee and P. J. Rossky, "A comparison of the structure and dynamics of liquid water at hydrophobic and hydrophilic surfaces—a molecular dynamics simulation study," J. Chem. Phys. **100**, 3334–3345 (1994).
[30]B. Jérôme and J. Commandeur, "Dynamics of glasses below the glass transition," Nature **386**, 589–592 (1997).
[31]S. Cerveny, F. Mallamace, J. Swenson, M. Vogel, and L. Xu, "Confined water as model of supercooled water," Chem. Rev. **116**, 7608–7625 (2016).
[32]S. Pezzotti, A. Serva, F. Sebastiani, F. S. Brigiano, D. R. Galimberti, L. Potier, S. Alfarano, G. Schwaab, M. Havenith, and M.-P. Gaigeot, "Molecular fingerprints of hydrophobicity at aqueous interfaces from theory and vibrational spectroscopies," J. Phys. Chem. Lett. **12**, 3827–3836 (2021).
[33]M. Dzugutov, "A universal scaling law for atomic diffusion in condensed matter," Nature **381**, 137–139 (1996).
[34]M. Dzugutov, "Anomalous slowing down in the metastable liquid of hard spheres," Phys. Rev. E **65**, 032501 (2002).
[35]E. G. D. Cohen, "Fifty years of kinetic theory," Physica A **194**, 229–257 (1993).
[36]P. G. De Gennes, "Liquid dynamics and inelastic scattering of neutrons," Physica **25**, 825–839 (1959).
[37]J. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, 1976).
[38]A. Baranyai and D. J. Evans, "Direct entropy calculation from computer simulation of liquids," Phys. Rev. A **40**, 3817–3822 (1989).
[39]H. J. Raveché, "Entropy and molecular correlation functions in open systems. I. Derivation," J. Chem. Phys. **55**, 2242–2250 (1971).
[40]R. D. Mountain and H. J. Raveché, "Entropy and molecular correlation functions in open systems. II two- and three-body correlations," J. Chem. Phys. **55**, 2250–2255 (1971).
[41]D. C. Wallace, "On the role of density fluctuations in the entropy of a fluid," J. Chem. Phys. **87**, 2282–2284 (1987).
[42]I. Yokoyama, "A relationship between excess entropy and diffusion coefficient for liquid metals near the melting point," Physica B **254**, 172–177 (1998).
[43]J. J. Hoyt, M. Asta, and B. Sadigh, "Test of the universal scaling law for the diffusion coefficient in liquid metals," Phys. Rev. Lett. **85**, 594–597 (2000).
[44]C. Herrero, M. Pauletti, G. Tocci, M. Iannuzzi, and L. Joly, "Connection between water's dynamical and structural properties: Insights from ab initio simulations," Proc. Natl. Acad. Sci. U. S. A. **119**, e2121641119 (2022).
[45]M. Dzugutov, E. Aurell, and A. Vulpiani, "Universal relation between the Kolmogorov-Sinai entropy and the thermodynamical entropy in simple liquids," Phys. Rev. Lett. **81**, 1762–1765 (1998).
[46]M. J. Abraham, T. Mutola, R. Schultz *et al.*, "GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers," Orig. Software Publ. **1**, 19–25 (2015).
[47]G. Tribello, M. Bonomi, D. Branduardi, C. Camilloni, and G. Bussi, "PLUMED 2: New feathers for an old bird," Comput. Phys. Commun. **185**, 604 (2014).
[48]A. P. Willard and D. Chandler, "The molecular structure of the interface between water and a hydrophobic substrate is liquid-vapor like," J. Chem. Phys. **141**(8), 18C519 (2014).
[49]P. Liu, E. Harder, and B. J. Berne, "On the calculation of diffusion coefficients in confined fluids and interfaces with an application to the liquid–vapor interface of water," J. Phys. Chem. B **108**, 6595–6602 (2004).
[50]Y. Rosenfeld, "Relation between the transport coefficients and the internal entropy of simple systems," Phys. Rev. A **15**, 2545–2549 (1977).
[51]M. Dzugutov, "addendum: A universal scaling law for atomic diffusion in condensed matter," Nature **411**, 720 (2001).
[52]B. N. J. Persson, *Sliding Friction: Physical Principles and Applications* (Springer Link, 2000).