Quantifying Density Fluctuations in Water at a Hydrophobic Surface: Evidence for Critical Drying

Robert Evans and Nigel B. Wilding

H. H. Wills Physics Laboratory, University of Bristol, Royal Fort, Bristol BS8 1TL, United Kingdom
Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom

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Employing smart Monte Carlo sampling techniques within the grand canonical ensemble, we investigate the properties of water at a model hydrophobic substrate. By reducing the strength of substrate-water attraction, we find that fluctuations in the local number density, quantified by a rigorous definition of the local compressibility \( \chi(z) \), increase rapidly for distances \( z \) within one or two molecular diameters from the substrate as the degree of hydrophobicity, measured by the macroscopic contact angle \( \theta \), increases. Our simulations provide evidence for a continuous (critical) drying transition as the substrate-water interaction becomes very weak: \( \cos(\theta) \to -1 \). We speculate that the existence of such a transition might account for earlier simulation observations of strongly enhanced density fluctuations.

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All physical scientists would agree that for water at a flat substrate a contact angle \( \theta > 90° \) defines the substrate as hydrophobic. For such values, Young’s equation implies that the substrate-vapor interfacial tension is lower than the substrate-liquid tension; i.e., the substrate prefers vapor to liquid. \( \theta \) is determined by surface chemistry, which in turn determines the strength and range of substrate-fluid interactions. A key question, much discussed by the chemical physics communities, is whether there is an effective indicator of local ordering of water, manifest at microscopic distances from the substrate, which might correlate with the degree of hydrophobicity, as measured by the macroscopic thermodynamic quantity \( \theta \). Quantifying the character and spatial extent of water ordering at hydrophobic entities is important across several disciplines, ranging from applied physics and materials science, where understanding slip lengths of water, shown to be correlated with substrate hydrophobicity, is crucial in microfluidics [1] and to biophysical processes such as protein folding and micelle and membrane formation [2].

Many studies have focused on the average one-body density, i.e., the density profile of oxygen atoms near the substrate. Experimentally, this is difficult to measure, and several conflicting results were reported. Nevertheless, by 2009, a consensus emerged from x-ray reflectivity measurements that for water near a variety of hydrophobic self-assembled monolayers (SAMs), there is a region of density depletion corresponding to only a fraction of a water monolayer [3–5]. This was challenged by Chattopadhyay et al. [6], who reported larger depletion lengths, increasing with \( \theta \), for water at fluoroalkylsilane SAMs. For the largest contact angle \( \theta = 120° \), the depletion length was 8 Å, corresponding to about three water layers.

However, in a reanalysis [7] of the x-ray reflectivity data of Ref. [6], it was argued that such a large hydrophobic gap is likely to be an artefact of the data analysis that was used. This is disputed [8]. Certainly such large depletion lengths are at odds with results of many computer simulations of water models, where the thickness of the depleted density region varies typically between 1.5 Å and 2.0 Å for \( \theta \) between about 110° and 130° [9].

Other simulation studies have focused on the density fluctuations of water at model hydrophobic substrates, arguing that some measure of the local compressibility might provide a better indicator of hydrophobicity than does the local density profile. The group of Garde [10] takes this stance, and the review by Jamadagni et al. [11] places their work in the context of biomolecular systems. Chandler and co-workers [12–14] and Mittal and Hummer [15] also emphasize that density fluctuations can be enhanced at hydrophobic substrates. Although these studies identify some underlying phenomenology, the various measures of the local compressibility introduced are ad hoc. In particular, these do not correspond to integrals over density correlation functions in the inhomogeneous liquid. Clear insights into the nature of the underlying fluctuations require such a measure [16]. Choice of ensemble is important. Most members of the community simulating water choose not to work grand canonically. In most real interfacial situations there is a reservoir, and it is natural to vary the chemical potential \( \mu \) of the liquid. Following a recent analysis [22] of density fluctuations in a Lennard-Jones (LJ) liquid at a planar substrate (wall), we argue that the most appropriate definition [16] of the local compressibility, for a fixed confining volume, is

\[
\chi(z) \equiv \frac{(\partial \rho(z)/\partial \mu)_T}{\kappa_f},
\]

where \( \rho(z) \) is the average one-body density, \( z \) is the distance normal to the substrate, and the temperature \( T \) is fixed. For a bulk fluid with constant density \( \rho_b \), \( \chi(z) \equiv \chi_b = \rho_b^2 \kappa_f \), where \( \kappa_f \) is the isothermal compressibility.
The definition (1) is consistent with $\chi(z)$ as an integral over the density-density correlation function and yields a unique fluctuation formula for this quantity [see Eqs. (8) and (9) of [16]]. In Ref. [22] it was shown using classical density functional theory (DFT) that for $z$ close to the substrate $\chi(z)/\chi_b$ becomes large as the substrate becomes more solvophobic; i.e., $\theta$ increases. The effects are not small: for $\theta \sim 160^\circ$, the ratio is about 25.

In this Letter, we determine the local compressibility of the extended simple point charge (SPC/E) model of water [23] near a planar substrate. On reducing the strength of substrate-water attraction, thereby increasing the hydrophobicity as measured by $\theta$, we find $\chi(z)$ increases in a similar fashion to the LJ case [22]. We focus on the approach to complete drying, $\cos(\theta) \rightarrow -1$ at bulk vapor-liquid coexistence $\mu = \mu_{\text{co}}$. Determining the nature of this transition continues to be challenging, even for simple fluids at solvophobic substrates. Using smart sampling techniques within Grand Canonical Monte Carlo (GCMC) simulations, we find evidence for a critical drying transition in SPC/E water at a weakly attractive substrate. We note that recent molecular dynamics (MD) simulations [14,24] of the same water model also investigate very weak substrate-water attraction. Although both studies attempt to link the growth of density fluctuations to increasing $\theta$, neither simulation measures $\theta$ accurately so proximity to the drying point is uncertain. Moreover, neither makes explicit the possibility of a critical drying transition. We argue the latter is key to understanding the properties of water models in the extreme hydrophobic regime and, in particular, the enhanced density fluctuations that are observed.

We choose SPC/E as a simple but realistic model of water, known to provide a reasonable account of bulk vapor-liquid coexistence and the vapor-liquid surface tension of real water [25,26]. Moreover, this model has often been employed in simulations of water at hydrophobic substrates; for examples of MD studies, see Refs. [10,14,24,27], and for GCMC studies, see Refs. [25,28–30]. Kumar and Errington employ simulation techniques similar to the present, but they do not measure $\chi(z)$; i.e., they do not access local density fluctuations. Rather, they measure [28] the surface excess compressibility $\chi_{\text{ext}}$, which is an integrated measure of excess density fluctuations throughout the system [16,22,31].

Our simulations were performed at $T = 298$ K. Since liquid water at room temperature is too dense for standard GCMC simulations to operate effectively, smart sampling techniques were implemented. Configurational bias MC simulations were used to insert, delete, translate, and rotate molecules [32], while Transition Matrix MC [33], Multicanonical Sampling [34], and Histogram Reweighting [35] were deployed to smoothly connect the vapor and liquid regions of configuration space. Together, these methods allowed us to simulate modest system sizes of order a few hundred water molecules very accurately. Although MD simulations typically deal with greater numbers of molecules, the GCE is the appropriate ensemble for accurately studying $\chi(z)$ and thermodynamic quantities such as $\cos(\theta)$ and surface phase behavior because it permits direct study of the fluctuations which characterize phase transitions. As these fluctuations occur on the scale of the system itself, the GCE is less afflicted by finite-size effects than other simulation ensembles.

We consider two simulation setups: (i) a fully periodic cubic box of volume $V = L^3$ and (ii) a semiperiodic cuboidal slit geometry of volume $V = L^2D$, in which the oxygen atoms interact with a pair of symmetry-breaking walls separated by distance $D$. For the latter geometry, the single wall-oxygen potential takes the form

$$V_s(z) = \frac{\alpha}{2} \left\{ \frac{1}{5} (\sigma_{wf}/z)^5 - (\sigma_{wf}/z)^3 \right\},$$

where $\sigma_{wf}$ is the wall-fluid interaction strength and $z$ is the distance from the wall. $\alpha$ is a constant that sets the unit of energy (see Supplemental Material [16]), while $\sigma_{wf}$ sets the length scale for wall-fluid interactions, which we assigned to be 3.5 Å, in accordance with previous studies [28].

The choice of $\sigma_{wf}$ controls the degree of hydrophobicity and hence the contact angle $\theta$. Our use of the GCE permits us to calculate $\theta$ directly from Young’s equation,

$$\gamma_{vl}(\cos(\theta)) = \gamma_{wv} - \gamma_{wl}.\quad (2)$$

Here $\gamma_{vl}$ is the vapor-liquid interfacial tension, and $\gamma_{wv}$ and $\gamma_{wl}$ are the wall-vapor and wall-liquid interfacial tensions, respectively. Provided one can calculate $\gamma_{vl}$ and $\gamma_{wv} - \gamma_{wl}$ at $\mu = \mu_{\text{co}}$, $\cos(\theta)$ is given. Both quantities are directly obtainable from measurements of the probability distribution $p(\rho)$ of the fluctuating molecular number density $\rho = N/V$ in the appropriate simulation geometry. Specifically, studies of $p(\rho)$ in the fully periodic system allow estimates of both $\mu_{\text{co}}$ and $\gamma_{vl}$, while studies of $p(\rho)$ in the slit geometry allow measurements of $\gamma_{wv} - \gamma_{wl}$.

For the periodic system at vapor-liquid coexistence, $p(\rho)$ exhibits a pair of equally weighted peaks [36] separated by a flat probability “valley.” The low- and high-density peaks correspond to pure vapor and liquid phase states, respectively, while the flat valley corresponds to liquid-slab configurations in which a pair of liquid-vapor interfaces align parallel to one face of the simulation box. Since in the probability valley $p_{\text{min}}$ is typically many decades smaller than the peak probabilities $p_{\text{vap}}$ and $p_{\text{liq}}$, standard sampling cannot plumb the valley depth. For this reason, Transition Matrix and Multicanonical MC techniques [33] were used to accumulate $p(\rho)$ in histogram form across the full range of density from vapor to liquid. Initially, $p(\rho)$ was determined for a near-coexistence state point. The distribution was then reweighted [35] with respect to $\mu$ to determine $\mu_{\text{co}}$ via the equal peak weight criterion. Once obtained, the coexistence form of $p(\rho)$ permits an estimate of $\gamma_{vl}$ [37,38]:

$$\gamma_{vl} = (2\beta L^2)^{-1} \ln(p_{\text{max}}/p_{\text{min}}),\quad (3)$$
where $\beta = (k_B T)^{-1}$ and $p_{\text{max}} \equiv p_{\text{vap}} = p_{\text{liq}}$ is the height of the pure phase peaks.

In a similar manner, estimates of $p(\rho)$ at coexistence were accumulated for the slit geometry at various $\epsilon_{w_f}$. The resulting histograms (Fig. 1) typically exhibit two peaks—one at low density corresponding to wall-vapor (i.e., vapor at the wall) configurations and another at high density corresponding to wall-liquid (liquid at the wall) configurations [39]. For a given $\epsilon_{w_f}$, $\gamma_{we} - \gamma_{wl}$ is calculated from the measured ratio of vapor and liquid peak heights in $p(\rho)$ [40]:

$$\gamma_{we} - \gamma_{wl} = -(2\beta L^2)^{-1} \ln(p_{\text{vap}}/p_{\text{liq}}). \quad (4)$$

We now discuss the pertinent features of Fig. 1, noting that $-\ln p(\rho)$ measures the grand potential of the fluid. For large values of $\epsilon_{w_f}$, wall-liquid configurations are much more probable than wall-vapor configurations. Indeed, for $\epsilon_{w_f} \approx 10.3$, we find $\cos(\theta) = 1$, corresponding to the transition to complete wetting by liquid water. Reducing $\epsilon_{w_f}$ below this value takes the system first into the partially wet (hydrophilic) regime for which $0^\circ < \theta < 90^\circ$. Thereafter, for $\epsilon_{w_f} \lesssim 6$, the system enters the partially dry (hydrophobic) regime in which $90^\circ < \theta < 180^\circ$ and where wall-vapor configurations are favored over wall-liquid ones [41].

As $\epsilon_{w_f}$ is reduced within the hydrophobic regime, $\epsilon_{w_f} < 6$, Fig. 1 shows that the height of the liquid peak diminishes progressively until it vanishes smoothly into a plateau in $\ln p(\rho)$ at a low wall strength, which for this system size is $\epsilon_{w_f} = 0.5(1)$. Interestingly, the vanishing of the liquid peak occurs precisely at the drying point $\cos(\theta) = -1$. This is clear from the dashed curve in Fig. 1(b), which shows the form of $\ln p(\rho)$ corresponding to the fully periodic system at coexistence, for the same value of $L$. The peak to valley separation in this plot is the same as the vapor to liquid peak separation in the slit system at $\epsilon_{w_f} = 0.5$. It follows from Eqs. (2)–(4) that the vanishing of the liquid peak in $\ln p(\rho)$ marks the drying point $\cos(\theta) = -1$.

The behavior of $\ln p(\rho)$ in the slit system as a function of $\epsilon_{w_f}$ reveals interesting qualitative differences between the nature of the approach to complete wetting $[\cos(\theta) \to 1]$ and to complete drying $[\cos(\theta) \to -1]$. In the former case, the wall-vapor configurations remain metastable at the transition, as evidenced by the presence of a vapor “peak” at the wetting wall strength $\epsilon_{w_f} = 10.3$. This signifies that the wetting transition of water is a first-order surface phase transition. In contrast, on approaching the drying point, the liquid peak vanishes smoothly into a plateau of constant probability. The distinction is borne out by a plot of $\cos(\theta) + 1$ versus $\epsilon_{w_f}$ calculated from (2) and shown in Fig. 2. We find that $\cos(\theta)$ approaches unity with a nonzero gradient denoting unambiguously a first-order wetting transition but appears to approach $-1$ tangentially. Such a scenario implies a continuous (critical) transition to drying.

FIG. 1 (color online). (a) The measured forms of $p(\rho)$ for a selection of values of $\epsilon_{w_f}$ spanning the range from wetting to drying; the contact angles $\theta$ are shown. The system size is $L = D = 20$ Å. (b) A closeup of the region close to the drying transition. Note the continuous erosion of the liquid peak as $\epsilon_{w_f}$ decreases. In (a) and (b), the dashed line is $p(\rho)$ for the periodic system with $L = 20$ Å.

FIG. 2. Estimates of $\cos(\theta) + 1$ as a function of $\epsilon_{w_f}$ spanning the region from wetting $\cos(\theta) = 1$ to drying $\cos(\theta) = -1$. Statistical uncertainties are smaller than symbol sizes.
The physical interpretation of the smooth erosion of the liquid peak on the approach to drying is that the free energy barrier attaching the liquid to the wall vanishes continuously. This allows the liquid layer to detach and be replaced by vapor. In our slit system, the emergent liquid-vapor interface fluctuates freely [cf., the plateau in $p(\rho)$ at $\epsilon_{wf} = 0.5$] until the liquid slab thickness decreases sufficiently that the system undergoes (capillary) evaporation. This interpretation is confirmed by measurements of the number density profile $\rho(z)$ of the oxygen atoms in the hydrophobic regime (Fig. 3). For medium-strength attractive wall-fluid interactions that give rise to “neutral” hydrophobicity, i.e., $\theta \approx 90^\circ$, the liquid density is high at the wall, and packing effects occur. The structure in the profiles decreases smoothly as $\epsilon_{wf}$ is reduced and a low-density vapor layer starts to appear near the wall, the thickness of which appears to grow continuously as drying is approached. The thickness of the vapor layer represents the order parameter for the drying transition \cite{42}.

The behavior of $\rho(z)$ on the approach to drying reveals the emergence of a vapor layer or density gap associated with hydrophobic surfaces. However, a much more sensitive and revealing measure of the degree of hydrophobicity is the compressibility profile $\chi(z)$ defined in (1), which provides a robust measure of local density fluctuations close to the wall. Accurate estimates of this quantity are readily obtained within the GCE by exploiting histogram reweighting to numerically differentiate the density profile $\rho(z|\mu)$. The measured forms of $\chi(z)$, normalized with respect to the bulk compressibility $\chi_b$ (i.e., the compressibility far from the wall), are presented in Fig. 4. These show that close to the wall, $\chi(z)/\chi_b$ grows rapidly as $\epsilon_{wf}$ is reduced toward the drying point, eventually exceeding its bulk value by nearly two orders of magnitude \cite{43}. This finding mirrors what is found in DFT calculations for the solvophobic regime in a Lennard-Jones system \cite{22} and reflects the development of a large transverse correlation length for density fluctuations as $\cos(\theta) \to -1$ \cite{16}. We note that there is a large enhancement in the local compressibility even for values of $\epsilon_{wf}$, which correspond to contact angles not much greater than $\theta = 90^\circ$ \cite{44}. This confirms the relevance of our findings for experimental studies on real smooth hydrophobic surfaces such as SAMs, where contact angles have a maximum value of about $130^\circ$.

In summary, we have shown that smart sampling within the GCE is a powerful approach for accurately characterizing the hydrophobic regime, including the approach to drying ($\theta \to 180^\circ$) in water. The local compressibility profile $\chi(z)$ is the proper statistical mechanics measure of local density fluctuations in fluids \cite{16}. When applied to water in contact with a hydrophobic substrate, $\chi(z)$ provides a sensitive indicator of how the microscopic structure near the substrate reflects the macroscopic contact angle $\theta$—much more so than the density profile $\rho(z)$ alone. In the drying limit, the order parameter (i.e., the thickness of the vapor layer) grows continuously but slowly with decreasing $\epsilon_{wf}$. In contrast, $\chi(z)$ grows rapidly and exceeds its bulk value by nearly two orders of magnitude over the range of $\epsilon_{wf}$ explored, indicating the growth of a large transverse correlation length \cite{16}. These findings point to drying in water at models of hydrophobic substrates as being a surface critical phenomenon. Indeed, separate simulation studies of drying in the Lennard-Jones system reproduce the phenomenology seen in our studies of water while increased system size permits the extraction of critical power law behavior \cite{45}. With these insights, one can rationalize and explain the observations of enhanced fluctuations in previous simulation studies of water near hydrophobic surfaces \cite{10,15,28}. We believe that these are attributable to the proximity of a surface critical point, i.e., the approach to a continuous drying

![FIG. 3](color online). Normalized number density profiles $\rho(z)$ for various values of $\epsilon_{wf}$ in the hydrophobic regime. $\rho_b$ is the bulk liquid density at $\mu_{cx}$.

![FIG. 4](color online). The normalized local compressibility $\chi(z)/\chi_b$ for a selection of values of $\epsilon_{wf}$. These correspond to the density profiles of Fig. 3.
transition, the effects of which extend throughout the hydrophobic regime but were not recognized previously.

Some of the simulations described here were performed on the Bath HPC Cluster. We thank Rob Jack and Kurt Binder for useful discussions.

[16] R. Evans and N. B. Wilding, Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.115.016103, which includes Refs. [17–21], provides (i) further details of simulations and (ii) a full discussion of how $\chi(z)$ is related to the density–density correlation function of the inhomogeneous fluid, a fluctuation formula for $\chi(z)$, and a brief summary of the measures of local compressibility introduced by other authors.
SUPPLEMENTARY MATERIAL

Simulation details

We used the Towhee molecular simulation package [32] to simulate SPC/E water. Electrostatic interactions were treated using the Ewald summation method, while Lennard-Jones interactions were truncated at 10 Å. Configurational bias Monte Carlo moves were used to insert, delete, translate and rotate molecules.

We considered two simulation setups: (i) a fully periodic cubic box of volume \( V = L^3 \); (ii) a semi-periodic cuboidal slit geometry of volume \( V = L^2D \), in which the oxygen atoms interact with a pair of symmetry-breaking walls separated by distance \( D \). In all cases we set \( L = D = 20 \) Å.

For the slit geometry, the single wall-Oxygen potential takes the form

\[
V_s(z) = \frac{2}{3}\pi \epsilon_{wf} \sigma_{wf}^3 \rho_{wall} \left( \frac{2}{15} (\sigma_{wf}/z)^9 - (\sigma_{wf}/z)^3 \right),
\]

where \( \epsilon_{wf} \) is the wall-fluid interaction strength and \( z \) is the perpendicular distance from the wall. The length-scale for wall-oxygen interactions \( \sigma_{wf} \) was set equal to 3.5 Å, and the wall density \( \rho_{wall} \) was set equal to 1 Å\(^{-3} \). Then the prefactor is \( \alpha = 89.80 \epsilon_{wf} \). Converting, the prefactor becomes 0.7468\( \epsilon_{wf} \) kJ/mol, where \( \epsilon_{wf} \) is now dimensionless. \( V_s(z) \) was truncated at 15 Å. Water molecules interact with both walls so \( V_w = V_s(z) + V_s(D - z) \).

Local compressibility, transverse correlations and fluctuation formulae

In the Letter it is argued that \( \chi(z) \), defined by Eq. (1), provides the most appropriate formal and computationally efficacious measure of a local compressibility. Here we explain why this is the case. Key to understanding density fluctuations at a substrate is the density-density correlation function of the inhomogeneous fluid. For a (planar) wall-fluid potential \( V_s(z) \), the density profile \( \rho(z) \) varies only in the direction \( z \) perpendicular to the wall and the density-density correlation function takes the form:

\[
G(r_1, r_2) \equiv \langle \hat{\rho}(r_1) - \langle \hat{\rho}(r_1) \rangle \rangle \langle \hat{\rho}(r_2) - \langle \hat{\rho}(r_2) \rangle \rangle = G(z_1, z_2; R),
\]

where \( R = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2} \) is the transverse separation between the particles (molecules), \( \hat{\rho}(r) = \sum_{i=1}^{N} \delta(r - r_i) \) is the particle density operator and the brackets \( \langle \rangle \) denote a grand canonical (GCE) average. We define the local, or transverse, structure factor as

\[
S(z_1; q) = \int_{-\infty}^{\infty} dz_2 G(z_1, z_2; q),
\]

where we have taken a Fourier transform w.r.t. \( R \), i.e. \( q \) is the transverse wavenumber. This transverse structure factor was introduced in several early studies of wetting and drying transitions in simple Lennard-Jones type fluids [17-19] as it provides a measure of the strength and range of transverse correlations for values of \( z \) ranging from close to the wall to \( l \), the thickness of the wetting, or drying, film. For example, in an early DFT treatment [18] Ornstein-Zernike behaviour was invoked for small \( q \):

\[
S(z; q) \approx \frac{S(z; 0)}{1 + \xi_q^2 q^2}
\]

and the transverse correlation length \( \xi_q \) was identified. In this and in subsequent DFT work [42] the divergence of \( \xi_q \) on approaching wetting and drying criticality was analyzed in detail.

It is straightforward to show [17-19,42] that \( \chi(z) \) is proportional to the \( q = 0 \) limit of (6), i.e.

\[
\chi(z) \equiv \left( \frac{\partial \rho(z)}{\partial \mu} \right)_T = \beta S(z; 0) = \beta \int_{-\infty}^{\infty} dz_2 \int dR G(z_1, z_2; R).
\]

Thus \( \chi(z) \) is the integral of \( G \) performed over the range of one normal coordinate and over that of all transverse coordinates. Eq. (8) can be re-expressed in a fluctuation formula obtained by first differentiating the grand partition function w.r.t. an external potential and then differentiating w.r.t. chemical potential:

\[
\chi(z) = \beta \langle N \hat{\rho}(r) - \langle N \rangle \langle \hat{\rho}(r) \rangle \rangle
\]

where \( N = \int d\vec{r} \langle \hat{\rho}(r) \rangle \) is the number of particles. Clearly \( \chi(z) \) correlates the local number density at \( z \) with the total number of particles in the system.

Integrating Eq. (8) over \( z \) and subtracting the bulk contribution yields the surface compressibility sum rule [19,20,42]:

\[
\chi_{ex} \equiv \left( \frac{\partial \Gamma_{ex}}{\partial \mu} \right)_T = \int_{0}^{\infty} dz \left[ \chi(z) - \chi_b \right] = \int_{0}^{\infty} dz \left[ \beta S(z; 0) - \chi_b \right]
\]

where \( \Gamma_{ex} = \int_{0}^{\infty} dz [\rho(z) - \rho_b] \) is the Gibbs excess adsorption and for simplicity we assume the fluid is adsorbed at
a single wall with $V_s(z)$ chosen so that $\rho(z) = 0, z < 0$. Extension to two walls is immediate. The fluctuation formula corresponding to the surface excess compressibility $\chi_{ex}$ is [22,31]:

$$\chi_{ex} = \frac{\beta}{A} \left[ (\langle N^2 \rangle - \langle N \rangle^2) - (\langle N^2_h \rangle - \langle N_h \rangle^2) \right], \quad (11)$$

and it is implied that the surface area of the wall $A \to \infty$. The first term in (11) is the mean-square fluctuation of the total number of particles which must be positive, while the second is the corresponding quantity for the bulk fluid at the same inverse temperature $\beta$ and chemical potential $\mu$. Bratko and co-workers [29,30] calculate the first term in GCMC simulations of SPC/E water. Kumar and Errington [28] calculate the difference Eq. (11). Neither computes the local quantity $\chi(z)$ which provides the crucial information about the spatial dependence of fluctuations that we focus upon here. In Fig. 5 we illustrate further the pronounced variation of $\chi(z)$ with increasing hydrophobicity by plotting $\chi_{max}$, the maximum of $\chi(z)$, versus $\cos(\theta)$. It is instructive to compare these results for SPC/E water with the corresponding ones for a LJ liquid calculated using DFT (see Fig. 5 of Ref. [22]). Although the variation with $\cos(\theta)$ away from drying is similar, ref. [22] did not investigate the approach to critical drying $\cos(\theta) = -1$ where we clearly observe a rapid growth in $\chi_{max}$.

As mentioned in the Letter and in Ref. [22], other authors choose different ways to define a local compressibility. In Eq. (1) of Ref. [10] the local compressibility is defined as $\rho(z)^{-1} \left( \partial \rho(z)/\partial P \right)_T$. We refer to the pressure $P$ to be $P(\mu)$, that of a reservoir free to exchange particles with the confined fluid, then this definition would yield the same information as our $\chi(z)$. However, it emerged from the discussion following presentation of Ref. [10] that in the studies performed by Garde’s group, $P$ is taken to be the normal component of the pressure tensor of the confined fluid. Thus our definition differs from theirs. Their local compressibility does not correspond to an integral such as Eq. (8). Nor does the integral over their local compressibility satisfy a sum rule such as Eq. (10). The latter pertains strictly to the GCE. The recent paper of Willard and Chandler [14] introduces a further measure of the strength of local number density fluctuations in characterizing results of MD simulations for SPC/E water near planar substrates. Specifically they plot in their Fig. 3 results for the quantity $\langle [N^2(z)] - \langle N(z) \rangle^2 \rangle/\langle N(z) \rangle$ for decreasing strengths of wall-fluid attraction. Here $N(z)$ is the number of water molecules in a spherical probe volume, chosen arbitrarily to have radius $3\AA$, and centred at a distance $z$ from the wall. This quantity is essentially the same as that termed $\chi_{fl}(z)$ in Ref. [10]. Although this quantity is somewhat analogous to our $\chi(z)/\rho(z)$ [22] it is certainly not identical. It does not correspond to an integral over a density-density correlation function and is a much less robust measure of fluctuations near a hydrophobic or solvophobic substrate. Making the appropriate definition of, and subsequently determining, the local compressibility is important particularly when characterising critical wetting and drying. This was recognized in the early study [18] and explicitly in Refs [21,42] where sum rules, involving integrals over $\chi(z)$, were used to develop relationships between critical exponents. These have been exploited in our simulation study of critical drying in the Lennard-Jones system [45].

![Fig. 5](image-url)