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# Quantifying density fluctuations in water at a hydrophobic surface: evidence for critical drying

Robert Evans<sup>1</sup> and Nigel B. Wilding<sup>2</sup>

<sup>1</sup>*H. H. Wills Physics Laboratory, University of Bristol, Royal Fort, Bristol BS8 1TL, United Kingdom*

<sup>2</sup>*Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom*

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 1 or 2 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:  $\cos(\theta) \rightarrow -1$ . We speculate that the existence of such a transition might account for earlier simulation observations of strongly enhanced density fluctuations.

All physical scientists would agree that for water at a flat substrate a contact angle  $\theta > 90^\circ$  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], to bio-physical processes such as protein-folding and micelle and membrane formation [2]. Many studies have focussed 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  $\theta = 120^\circ$  the depletion length was  $8\text{\AA}$ , corresponding to about three water layers. However, in a re-analysis [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  $1.5 - 2.0\text{\AA}$  for  $\theta$  between about  $110^\circ$  and  $130^\circ$  [9].

Other simulation studies have focussed 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 bio-molecular 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 requires 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 [17] 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

$$\chi(z) \equiv (\partial\rho(z)/\partial\mu)_T, \quad (1)$$

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  $\rho_b$ ,  $\chi(z) \equiv \chi_b = \rho_b^2 \kappa_T$ , where  $\kappa_T$  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. (8,9) of [16]. In ref. [17] 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 [18] 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 [17]. We focus on the approach to complete drying,  $\cos(\theta) \rightarrow -1$  at bulk vapor-liquid coexistence  $\mu = \mu_{cx}$ . 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 MD simulations [14, 19] 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 [20, 21]. Moreover, this model has often been employed in simulations of water at hydrophobic substrates; for examples of MD studies see refs. [10, 14, 19, 22] and for GCMC studies see refs. [20, 23–25]. 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 [23] the surface excess compressibility  $\chi_{ex}$  which is an *integrated* measure of ‘excess’ density fluctuations throughout the system [16, 17, 26]

Our simulations were performed at  $T = 298\text{K}$ . Since liquid water at room temperature is too dense for standard GCMC to operate effectively, smart sampling techniques were implemented. Configurational Bias MC was used to insert, delete, translate and rotate molecules [27], while Transition Matrix MC [28], Multicanonical Sampling [29] and Histogram Reweighting [30] 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 behaviour because it permits direct study of the fluctuations which characterise 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  $V = L^3$ ; (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  $D$ . For the latter geometry, the single wall-oxygen potential takes the form  $V_s(z) = \alpha\epsilon_{wf}[2/15(\sigma_{wf}/z)^9 - (\sigma_{wf}/z)^3]$ , where  $\epsilon_{wf}$  is the wall-fluid interaction strength and  $z$  is the distance from the wall.  $\alpha$  is a constant, the choice which sets the units of energy (see Supplementary Material [16]), while  $\sigma_{wf}$  sets the length scale for wall-fluid interactions which we assigned to be  $3.5\text{\AA}$ , in accordance with previous studies [23].

The choice of  $\epsilon_{wf}$  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  $\mu = \mu_{cx}$ ,  $\cos(\theta)$  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  $\mu_{cx}$  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 [31] 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  $p_{\min}$  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 [28] 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 [30] with respect to  $\mu$  to determine  $\mu_{cx}$  via the equal peak weight criterion. Once obtained, the coexistence form of  $p(\rho)$  permits an estimate of  $\gamma_{vl}$  [32, 33]:

$$\gamma_{vl} = (2\beta L^2)^{-1} \ln(p_{\max}/p_{\min}), \quad (3)$$

where  $\beta = (k_B T)^{-1}$  and  $p_{\max} \equiv p_{\text{vap}} = p_{\text{liq}}$  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  $\epsilon_{wf}$ .

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 [34]. For a given  $\epsilon_{wf}$ ,  $\gamma_{wv} - \gamma_{wl}$  is calculated from the measured ratio of vapor and liquid peak heights in  $p(\rho)$  [35]:

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

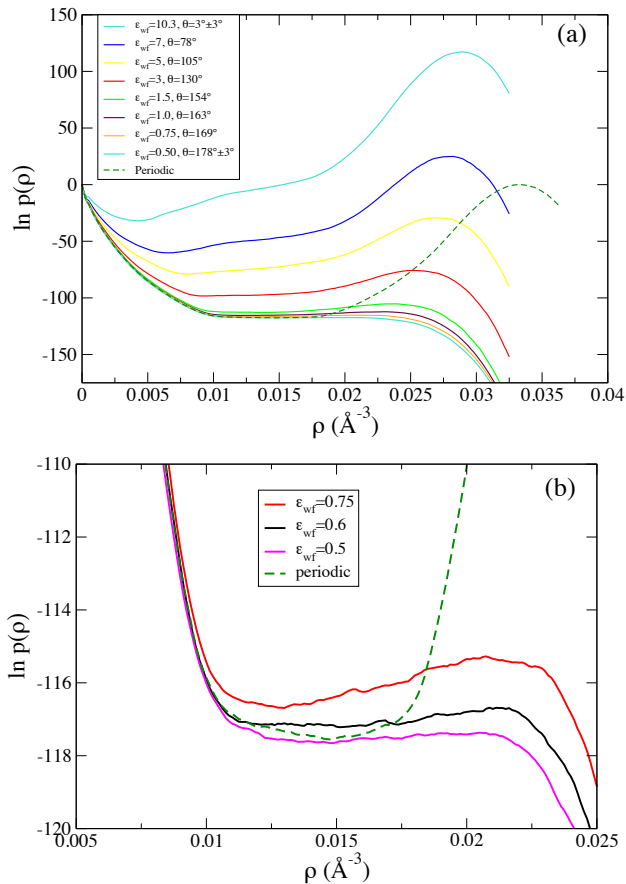


FIG. 1. (Color online). (a) The measured forms of  $p(\rho)$  for a selection of values of  $\epsilon_{wf}$  spanning the range from wetting to drying; the contact angles  $\theta$  are shown. The system size is  $L = D = 20\text{\AA}$ . (b) A closeup of the region close to the drying transition. Note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

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  $\epsilon_{wf}$ , wall-liquid configurations are much more probable than wall-vapor configurations. Indeed for  $\epsilon_{wf} \approx 10.3$ , we find  $\cos(\theta) = 1$ , corresponding to the transition to complete wetting by liquid water. Reducing  $\epsilon_{wf}$  below this value takes the system first into the partially wet (hydrophilic) regime for which  $0^\circ < \theta < 90^\circ$ . Thereafter, for  $\epsilon_{wf} \lesssim 6$ , the system enters the partially dry (hydrophobic) regime in which

$90^\circ < \theta < 180^\circ$  and where wall-vapor configurations are favoured over wall-liquid ones [36].

As  $\epsilon_{wf}$  is reduced within the hydrophobic regime,  $\epsilon_{wf} < 6$ , 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  $\epsilon_{wf} = 0.5(1)$ . 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  $\epsilon_{wf} = 0.5$ . 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 behaviour of  $\ln p(\rho)$  in the slit system as a function of  $\epsilon_{wf}$  reveals interesting qualitative differences between the nature of the approach to complete wetting ( $\cos(\theta) \rightarrow 1$ ), and to complete drying ( $\cos(\theta) \rightarrow -1$ ). 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  $\epsilon_{wf} = 10.3$ . This signifies that the wetting transition of water is a first order surface phase transition. By 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  $\epsilon_{wf}$  calculated from (2) and shown in Fig. 2. We find that  $\cos(\theta)$  approaches unity with a non-zero gradient denoting unambiguously a first order wetting transition, but appears to approach  $-1$  tangentially. Such a scenario implies a continuous (critical) transition to drying.

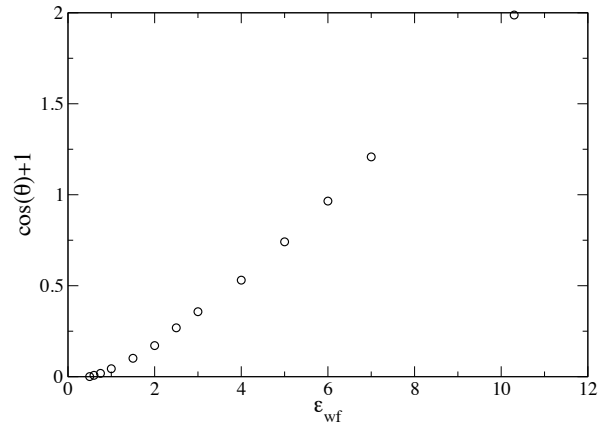


FIG. 2. Estimates of  $\cos(\theta) + 1$  as a function of  $\epsilon_{wf}$  spanning the region from wetting  $\cos(\theta) = 1$  to drying  $\cos(\theta) = -1$ . Statistical uncertainties are smaller than symbol sizes.

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 which give rise to ‘neutral’ hydrophobicity, i.e.  $\theta \sim 90^\circ$ , 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 [37].

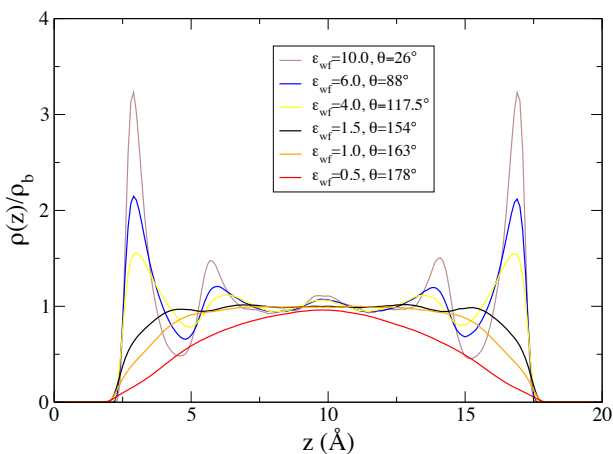


FIG. 3. (Color online). Normalized number density profiles  $\rho(z)$  for various values of  $\epsilon_{wf}$  in the hydrophobic regime.  $\rho_b$  is the bulk liquid density at  $\mu_{cx}$ .

The behaviour 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 towards the drying point, eventually exceeding its bulk value by nearly two orders of magnitude [38]. This finding mirrors what is found in DFT calculations of the solvophobic regime in a Lennard-Jones system [17], and reflects the development of a large transverse correlation length for density fluctuations as  $\cos(\theta) \rightarrow -1$  [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  $\theta = 90^\circ$  [39]. 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  $130^\circ$ .

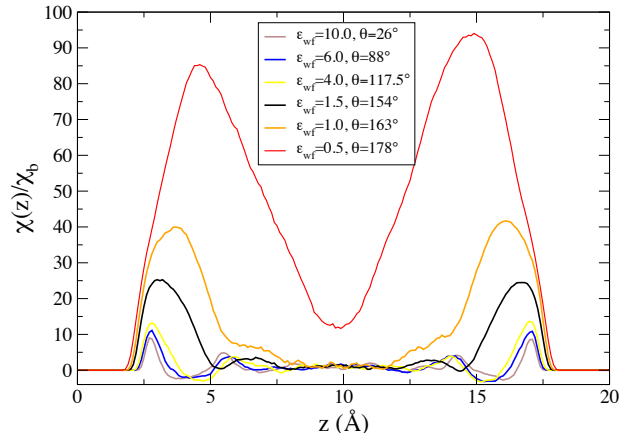


FIG. 4. (Color online). The normalized local compressibility  $\chi(x)/\chi_b$  for a selection of values of  $\epsilon_{wf}$ . These correspond to the density profiles of Fig. (3).

In summary, we have shown that smart sampling within the GCE is a powerful approach for accurately characterising the hydrophobic regime including the approach to drying ( $\theta \rightarrow 180^\circ$ ) in water. The local compressibility profile  $\chi(z)$  is the proper statistical mechanics measure of local density fluctuations in fluids [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 [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 whilst increased system size permits the extraction of critical power law behaviour [40]. With these insights, one can rationalize and explain the observations of enhanced fluctuations in previous simulation studies of water near hydrophobic surfaces [10–15, 23]. We believe that these are attributable to the proximity of a surface critical point i.e. the approach to a continuous drying transition, the effects of which extend throughout the hydrophobic regime but were not recognised previously.

Some of the simulations described here were performed

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