

### 2.4.5 Wetting and Drying Phase Transitions

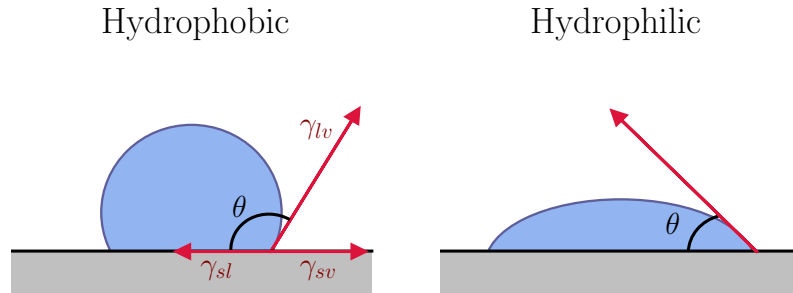
Consider a droplet of water on a surface, as shown in figure 2.3. Depending on the character of the surface, the droplet may be rounded or flat. This property can be quantified by considering the contact angle the droplet makes with the surface, denoted as  $\theta$ , and an expression for  $\theta$  can be derived by resolving the surface tension components of the three interfaces [49]. Doing so leads to Young's equation [41, 49, 50]

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (2.4.19)$$

where  $\gamma_{sv}$ ,  $\gamma_{sl}$  and  $\gamma_{lv}$  are the surfaces tensions of the surface-vapour, surface-liquid and liquid-vapour interfaces respectively, and are as shown in figure 2.3. The contact angle a droplet of water makes with a surface provides a definition for the affinity of the surface and water. Surfaces which have low affinity with water make obtuse contact angles, such that  $90^\circ < \theta < 180^\circ$  and are termed hydrophobic. Similarly, surfaces which have high affinity with water make acute contact angles, such that  $0^\circ < \theta < 90^\circ$ , and are termed hydrophilic.

From the definition of the contact angle, two interesting cases relating to  $|\cos \theta| = 1$  arise. In the first case, where  $\cos \theta = 1$  and therefore  $\theta = 0^\circ$ , the droplet of water completely covers the surface and Young's equation reduces to  $\gamma_{sl} = \gamma_{sv} - \gamma_{lv}$ . In the second case, where  $\cos \theta = -1$  and therefore  $\theta = 180^\circ$ , the droplet of water forms a perfect sphere which is no longer in contact with the surface. In this case, Young's equation reduces to  $\gamma_{sl} = \gamma_{sv} + \gamma_{lv}$ . The approach to these cases correspond to surface phase transitions, termed wetting and drying respectively, and represent the formation of a macroscopic layer of liquid or vapour at the surface [41, 49, 50].

The reasoning behind such a phase transition was first presented by Cahn [51], whose argument was based on the scaling of these surface tensions on the approach to the critical point of the bulk fluid. Cahn noted that, as  $T_c$  is approached from below, the liquid-vapour surface tension vanishes as  $\gamma_{lv} \sim (-t)^\mu$ , where  $t$  is the reduced temperature as defined in section 2.4.1 and  $\mu = (d-1)\nu$  is a critical exponent [50, 51]. For a fluid,  $d = 3$  and  $\nu \approx 0.63$  [47], therefore the critical exponent  $\mu \approx 1.26$ . In addition, Cahn argued that  $\gamma_{sv} - \gamma_{sl}$  should also vanish, as the liquid and vapour cease to be distinguishable at the bulk critical point.



**Figure 2.3:** Droplet of water on a surface. If the surface is hydrophobic, the contact angle the droplet makes with the surface,  $\theta$ , will be obtuse. If the surface is hydrophilic,  $\theta$  will be acute. The contact angle can be found by resolving the three surface tensions within the system, indicated by the arrows and denoted as  $\gamma$ .

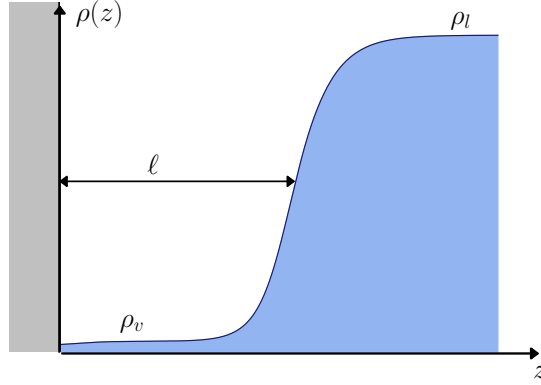
The similarity of the liquid and vapour phases in a near-critical fluid can be quantified by the order parameter  $(\rho_l - \rho_v)$ , which is known to vanish as  $(\rho_l - \rho_v) \sim (-t)^\beta$  on the approach to  $T_c$ , where  $\beta \approx 0.33$  for a bulk fluid [47]. Following Cahn's argument, the contact angle should therefore vanish as  $\cos \theta \sim (-t)^{\beta-\mu} = t^{-0.93}$ , which implies a divergence of  $\cos \theta$  on the approach to  $T_c$ . However, the contact angle is constrained to values of  $|\cos \theta| \leq 1$  and hence Cahn argued that there must exist a temperature,  $T_W < T_c$ , corresponding to  $\cos \theta = 1$ , for which the system undergoes a surface phase transition where the water fully wets the surface and after which the contact angle remains equal to  $0^\circ$  [51]. Similarly, in the case that  $\cos \theta = -1$ , a temperature  $T_D < T_c$  must exist in which a vapour fully wets the surface.

Around the same time Cahn made his thermodynamic argument, Ebner and Saam [52] provided numerical evidence for a surface phase transition by considering a model of an argon gas in contact with a solid  $\text{CO}_2$  surface. At low temperatures, a thin liquid film of argon was found to form at the  $\text{CO}_2$  surface. Upon raising the temperature, this thin adsorbed film suddenly transformed to a thick adsorbed film, in a surface phase transition now referred to as prewetting. Their results proved controversial, with subsequent numerical and simulation studies finding no evidence of such a transition [53, 54]. It was suggested that these discrepancies were due to the parameters at which Ebner and Saam had found the transition, as a later study using a similar method that found such a transition reported it to be at a much higher temperature and far closer to liquid-vapour coexistence [55].

Subsequent studies on wetting were also subject to much debate, particularly in regards to its nature. Cahn's original thermodynamic argument suggested that wetting was a first-order transition [51], evidence for which was provided in simulation studies of lattice gas models [56, 57]. In contrast, a microscopic theory of wetting based on a MFT van der Waals model of fluids by Sullivan [58] found that wetting was instead a critical phase transition. Later studies showed both types of wetting phase transition were possible [59, 60], and that the exact nature of the transition was strongly dependent on the comparative strengths of the substrate-fluid (sf) and fluid-fluid (ff) interactions, as well as the range over which each interaction extended [59–61]. These early studies focused almost exclusively on the case of wetting, as drying was viewed as the wetting of a surface by a vapour and therefore any arguments made for wetting were believed to be generally applicable to drying too [49, 58, 62]. Lattice gas studies took this idea further, as the particle-hole symmetry directly implied that wetting and drying were equivalent provided that the bulk fluid was replaced by a liquid in the latter and that the film formed was a vapour [61].

Whilst from a phenomenological perspective, wetting and drying are similar [49], it is now appreciated that they are distinct and that their nature may differ for a given substrate and fluid [1, 38]. As this work is concerned with hydrophobicity and therefore drying, the phenomenology is presented from this perspective, however replacing the drying temperature,  $T_D$ , with the wetting temperature,  $T_W$ , the bulk liquid with a bulk vapour, a vapour film with a liquid film and an oversaturation with an undersaturation in any of the following arguments will recover wetting, as presented in texts such as [41, 49, 50].

Consider a bulk liquid, of density  $\rho_l$ , in contact with an impenetrable substrate. If the



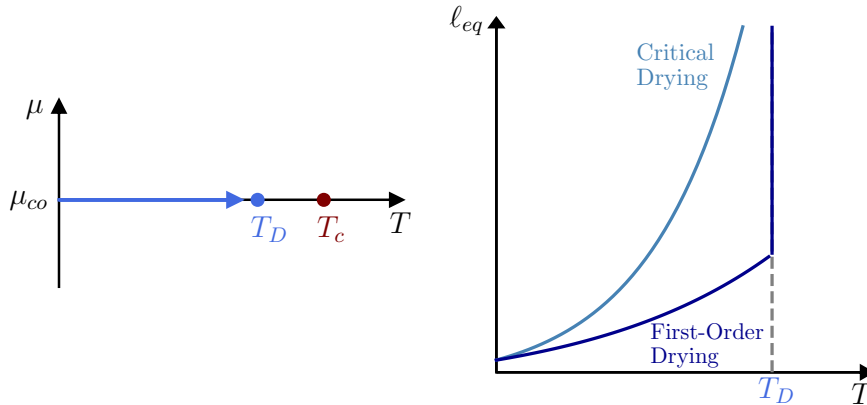
**Figure 2.4:** Illustration of the behaviour of a fluid, shown in blue, in contact with an impenetrable substrate, shown in grey. Near to drying, a film of vapour, of width  $\ell$ , forms at the surface. Here,  $\rho_l$  represents the density of the fluid, at coexistence, in its liquid phase, whilst  $\rho_v$  represents the density of the fluid, at coexistence, in its vapour phase.

liquid is at coexistence with its vapour phase, of density  $\rho_v$ , a film of vapour may form at the surface of the substrate [41, 49, 50]. Such a system is shown in figure 2.4, where the width of the vapour film is denoted by  $\ell$ . The adsorption of such a system can be found using equation (2.3.11), and will be of magnitude  $\Gamma \approx -\Delta\rho\ell A_{sv}$ , where  $\Delta\rho = (\rho_l - \rho_v)$  and  $A_{sv}$  is the surface area of the substrate-vapour interface. The adsorption can in fact be used to define the width of the film as [49]

$$\ell \equiv \frac{-\Gamma}{A_{sv}\Delta\rho} \quad (2.4.20)$$

If the system is at equilibrium, this also provides a definition for the equilibrium film width, denoted as  $\ell_{eq}$ .

Below  $T_D$ , the vapour film is microscopic, and hence  $\ell_{eq}$  is finite. However, as  $T_D$  is approached from below, the equilibrium width of the film grows and exactly at  $T_D$ , drying



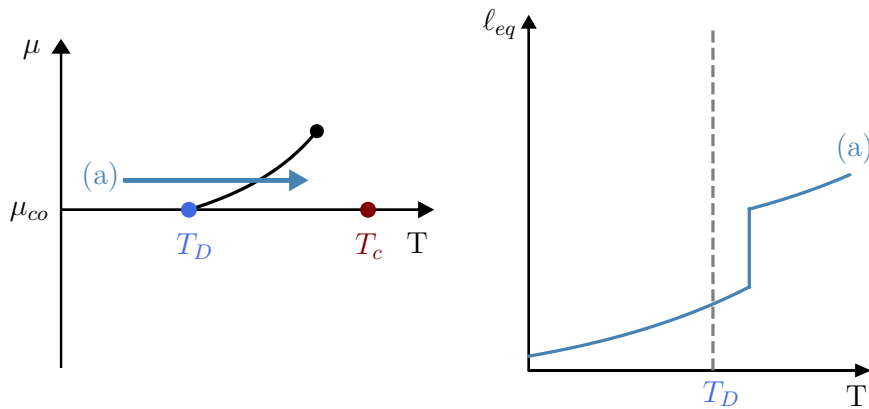
**Figure 2.5:** Examples of the behaviour of the equilibrium film width,  $\ell_{eq}$ , on the approach to the drying surface phase transition. Left: Illustration of path within parameter space corresponding to the approach to critical drying. Right: If the transition is critical, as  $T_D$  is approached from below at coexistence,  $\ell_{eq}$  will grow to a macroscopic width continuously. If the transition is first-order, then at  $T_D$ ,  $\ell_{eq}$  will jump discontinuously to a macroscopic film width. Note, the diagram on the left is purely illustrative, and does not reflect the true shape of the coexistence curve.

occurs. The vapour film then becomes macroscopic, which corresponds to the equilibrium film width becoming  $\ell_{eq} = \infty$ . This transition from a microscopic to macroscopic film width can either be first-order or critical. If first-order drying occurs, then  $\ell_{eq}$  becomes macroscopic discontinuously. If the transition is instead critical, the growth of  $\ell_{eq}$  is smooth and exactly at  $T_D$ ,  $\ell_{eq}$  diverges [41, 49, 50]. Each of these cases can be seen in figure 2.5.

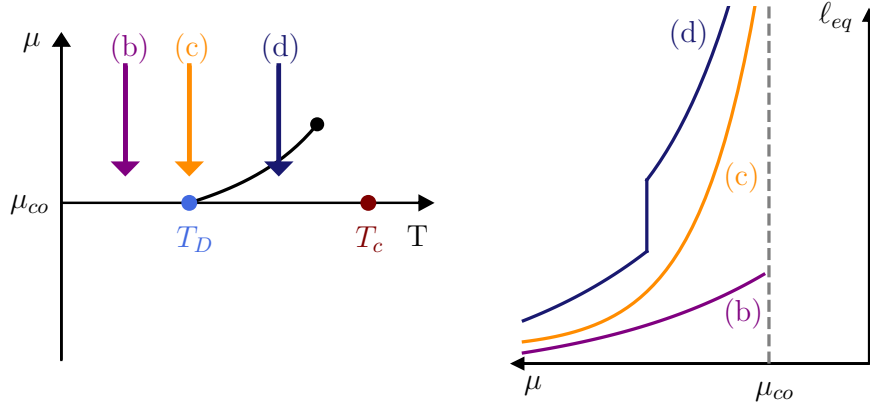
If the fluid exhibits a small oversaturation, which corresponds to  $\mu > \mu_{co}$ , then even as  $T_D$  is approached, the vapour film will remain finite [50]. If the drying transition is first-order, then it is possible for the fluid to undergo a different but related surface phase transition, called predrying, in which the vapour film transitions from a thin to thick width. These transitions are first-order, and their magnitude depletes as the oversaturation is increased. The locus of predrying transitions allows for the definition for the predrying line on the phase diagram. This terminates in a critical point, termed the predrying critical point, at which the transition between the thin and thick film widths becomes a smooth, rounded point of inflection [49, 50, 60].

In addition to first-order, critical and predrying, there exists one other way in which the vapour film may become macroscopic, which is termed complete drying. Complete drying specifically refers the divergence of the vapour film width as  $\mu_{co}$  is approached from an oversaturation, for temperatures  $T_D \leq T < T_c$ , and is always a continuous transition. The definition of complete drying also allows for the definition of incomplete drying. This refers to the microscopic nature of the film width, if  $\mu_{co}$  is approached from an oversaturation, however for  $T < T_D$  [50].

Examples of predrying, incomplete and complete drying can be seen in figures 2.6 and 2.7. Path (a) in figure 2.6 indicates predrying, as  $T$  is increased. Path (b) and (c) in figure 2.7 indicate incomplete and complete drying respectively. Path (d) in figure 2.7 indicates both predrying and complete drying, with a thin to thick film width transition occurring first, followed by a divergence in the film width as  $\mu_{co}$  is approached.



**Figure 2.6:** Illustration of the behaviour of  $\ell_{eq}$  if predrying occurs. If the fluid has a small oversaturation, it is possible that, at a temperature  $T > T_D$ , it will undergo a phase transition from a thin to a thick film width. This is known as predrying. The predrying line extends from  $T_D$  at the coexistence line, and terminates in a critical point. Note, the diagram on the left is purely illustrative, and does not reflect the true shape of the coexistence curve.

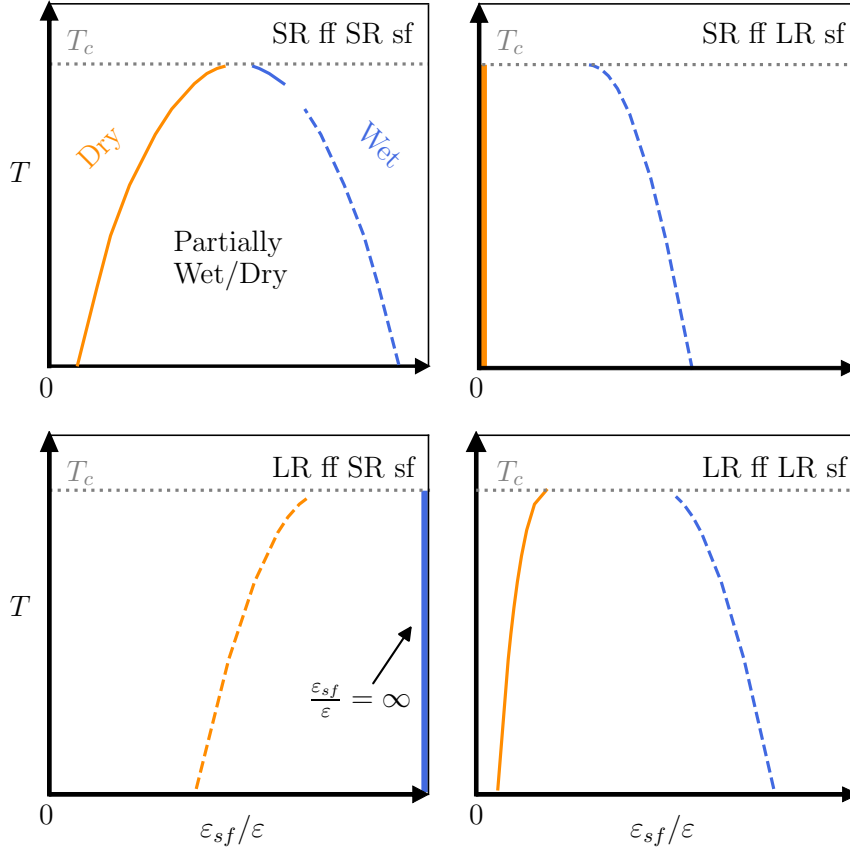


**Figure 2.7:** Illustration of the behaviour of  $\ell_{eq}$  (right) along different isotherms (left), as  $\mu_{co}$  is approached from above. Below  $T_D$ , indicated by (b), the vapour film grows, but remains microscopic. Exactly at  $T_D$ , indicated by (c), the equilibrium film width diverges continuously as  $\mu_{co}$  is approached, in a transition termed complete drying. Above  $T_D$ , as indicated by (d), two transitions may occur. As the isotherm crosses the predrying line, the vapour film width will transition discontinuously from a thin to a thick width. Then, as  $\mu_{co}$  is approached, the equilibrium film width will diverge continuously. Note, the diagram on the left is purely illustrative, and does not reflect the true shape of the coexistence curve.

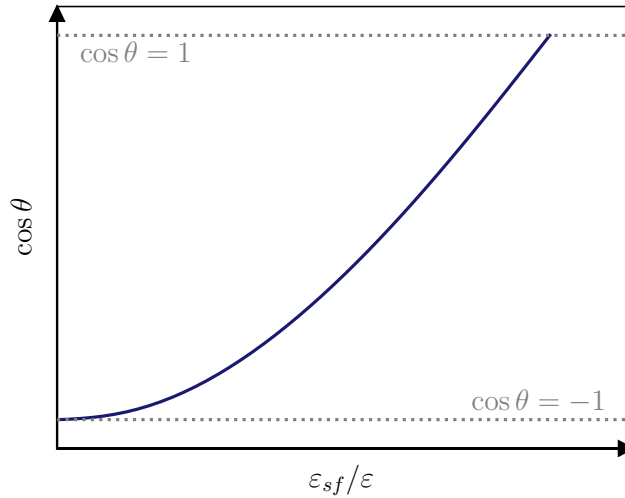
As was appreciated early in the study of wetting and drying, the order of the drying transition is determined by factors such as the relative strengths of the sf interaction, denoted  $\varepsilon_{sf}$ , and ff interaction, denoted by  $\varepsilon$ , and the range of such interactions [59–61]. The latter can be classified broadly as short-ranged (SR), which are typically exponential or finite ranged in nature, or long-ranged (LR), which are typically inverse power law in nature. Only recently have the orders of wetting and drying for various combinations of these been mapped out fully [38]. Figure 2.8 presents the current understanding of the nature of each combination. Notably, in many cases, drying is a critical surface phase transition, whilst wetting is first-order. This is specifically true for the typical interactions found in simulation (SR ff LR sf) and in experiment (LR ff LR sf). As predrying can only occur in systems which undergo first-order drying, this has the consequence that predrying is not normally possible.

The order of the wetting and drying transitions can be determined from the behaviour of  $\cos \theta$  on the approach to the transition, as  $\varepsilon_{sf}/\varepsilon$  is varied. Figure 2.9 shows this for the case of SR ff LR sf interactions.  $\cos \theta = -1$  is approached tangentially, indicating a smooth divergence and therefore a critical drying transition. In contrast,  $\cos \theta = 1$  is met with a discontinuous slope, indicating a discontinuous change in film width and therefore a first-order wetting transition [38].

Our current understanding of wetting and drying has mostly come about through MFT theoretical [51, 52, 60, 61], numerical [38] and simulation [56, 57] studies, and to date there is little experimental evidence confirming the orders and behaviours of these transitions. Of the studies which exist, most have utilised hydrocarbons in contact with a liquid surface, and have explored wetting transitions [63–67]. Despite the different type of surface, the physics remains the same and such studies have reported evidence of first-order wetting [64, 65], critical wetting [63, 65–67] and prewetting [66, 67].



**Figure 2.8:** Surface phase diagrams for systems with different combinations of short-ranged (SR) and long-ranged (LR) fluid-fluid (ff) and substrate-fluid (sf) interactions. In each case, the horizontal dotted grey line represents the critical temperature. Drying transitions are indicated in dark orange, whilst wetting transitions are indicated in light blue. Solid transition lines represent critical transitions, whilst dashed transition lines represent first-order transitions. In the case of SR ff SR sf interactions, the possible states of the system are labelled.



**Figure 2.9:** Examples of the variation of  $\cos \theta$  with  $\varepsilon_{sf}/\varepsilon$  for a system with SR ff LR sf interactions. The critical drying transition is indicated by the tangential approach to  $\cos \theta = -1$ . In contrast, the first-order wetting transition is indicated by the discontinuous slope on the approach to  $\cos \theta = 1$ .