## Must Thin-Thick Transitions Precede Long-Range Critical Wetting?

In a recent Letter Shahidzadeh *et al.* observe for hexane on water a sequence of two wetting transitions, induced by tuning the Hamaker constant $W$ [1]. Upon increasing the temperature $T$ a *first-order* transition between a thin (microscopic) and a thicker (mesoscopic) film takes place at $T_{w,1}$, and at $T_{w,c} > T_{w,1}$ a *critical* wetting transition occurs from a mesoscopic film to a thick (macroscopic) wetting layer. The authors conclude that probably the most important result of these experiments is that the two transition temperatures appear strongly coupled, possibly because both are directly connected to $W$. In this Comment we argue that this coupling is a coincidence rather than a necessity, and that only the critical wetting transition is directly connected to $W$.

The Cahn-Landau theory can reproduce the sequence of wetting transitions and explain it in terms of a competition between the short-range [$r < \mathcal{O}(\sigma)$] and long-range [$r \gg \mathcal{O}(\sigma)$] parts of the intermolecular forces [2,3], where $\sigma$ is a molecular size. The theory predicts that in order for long-range critical wetting (LRCW) to be possible, the short-range forces should induce *complete wetting* and the long-range forces should allow a change of sign of the Hamaker constant $W$, from opposing to favoring wetting. $W$ need not influence the first-order transition, the location of which is primarily determined by the short-range forces. In contrast, the behavior of $W$ is crucial to critical wetting.

The experiments on alkanes on water, and model calculations [4], indicate that LRCW is systematically preceded by a thin-thick transition. Is this a coincidence or a necessity? Answering this also helps to clarify another theoretically predicted transition, short-range critical wetting (SRCW), which has been invoked to explain a wetting transition near the consolute point in fluid mixtures [5]. Assuming that the transition is continuous, the presence or absence of a preceding thin-thick transition may help to distinguish SRCW from LRCW.

Employing Cahn-Landau theory we distinguish two cases, assuming that the short-range forces favor complete wetting and that LRCW occurs at $T_{w,c}$.

*Case 1.—The short-range forces alone would lead to a first-order wetting transition at* $T_{w,1} < T_{w,c}$. The theory that neglects the long-range forces then predicts a first-order transition from a thin film to a macroscopic wetting layer. Then the LRCW transition at $T_{w,c}$ is preceded by a thin-thick transition near $T_{w,1}$, which is the remnant of the first-order wetting transition that would occur at $T_{w,1}$ if the long-range forces were negligible. Whether or not $T_{w,1}$ is close to $T_{w,c}$ depends on the system. In order for the thin-thick transition to be observable, we need at least $T_{w,1} > T_{tr}$, where $T_{tr}$ is the triple-point temperature of the adsorbate. Otherwise, the short-range forces would lead to triple-point wetting [6], which is a continuous transition.

*Case 2.—The short-range forces alone would lead to a critical wetting transition at* $T_{w,2} < T_{w,c}$. SRCW is a continuous transition, predicted for systems with short-range forces and a wetting transition *close to the adsorbate critical point* $T_c$, if the surface-coupling enhancement is negative [7]. The latter is expected for adsorbed fluids. Including the long-range forces in the phase portraits shows that the thin film continuously becomes thicker, without discontinuity. Therefore, LRCW is not preceded by a thin-thick transition. An exception is possible when the short-range forces lead to a thin-thick transition between two *microscopic* films, preceding SRCW [8]. Then LRCW is preceded by the remnant of that (weak) thin-thick transition.

In conclusion, LRCW is preceded by a thin-thick transition from a microscopic to a mesoscopic film, if the system in which only the short-range part of the forces is taken into account displays a *first-order* wetting transition at $T_{w,1}$ not far below $T_{w,c}$. Note that this can help distinguish SRCW from LRCW in van der Waals fluids. A thin-thick transition to a mesoscopic film preceding the critical wetting transition indicates LRCW. Conversely, the absence of a thin-thick transition before a critical wetting transition near $T_c$ is compatible with SRCW, but to rule out LRCW other evidence must be supplied (e.g., the sign of $W$ and the critical exponents).

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