Quasiwetting and Critical-Point Leaps

In a recent Letter, Parry and Evans (PE) discuss wetting phenomena and bulk phase equilibria in confined systems with opposing walls (one wall wets, the other dries). They conclude that bulk two-phase coexistence is destroyed if the surface fields of the walls are strong enough to cause complete wetting for one wall and complete drying for the other. In other words, they propose that the bulk critical point $T_{c, \text{bulk}}$ is shifted all the way towards the wetting transition point $T_w$ as soon as the wall separation $L$ is finite. The same surmise was put forward in an earlier paper by Brochard-Wyart and de Gennes.

More precisely, PE argue that for a fluid exhibiting a critical wetting transition for $L = \infty$, coexistence ends at a critical point $T_c(L)$ that is very close to $T_w$ (the distance $T_w - T_c(L)$ being of order $L^{-1/\beta_2}$, where $\beta_2$ is the exponent describing the growth of a wetting film). PE infer that the standard finite-size scaling for the bulk critical-point shift is not applicable to $T_{c, \text{bulk}} - T_c(L)$ in this system with opposing walls. Instead they propose an alternative scaling ansatz for $T_w - T_c(L)$ (see above), but continue to interpret $T_c(L)$ as the shifted bulk critical point.

We begin by remarking that the $T_c(L)$ studied PE converges to $T_w$ and not to $T_{c, \text{bulk}}$ for $L \to \infty$ (at fixed nonzero surface fields). This means that if $T_c(L)$ is interpreted as the shifted bulk critical point (as PE propose), the critical-point shift would be discontinuous at $L = \infty$. Clearly, this critical-point leap is curious since it violates standard finite-size scaling considerations. We are skeptical about this alleged novel mechanism and question PE’s interpretation of $T_c(L)$ being the shifted bulk critical point.

Our calculations show that, in the same Landau theory that PE used, the familiar first-order, critical, and tricritical wetting transitions (in the semi-infinite system, for $L = \infty$) are shifted to (near) first-order, critical, and tricritical quasiwetting, respectively, for finite $L$.

The quasiwetting transitions, $T_w(L)$, converge to the wetting transitions at $T_w$ for $L \to \infty$. We note that the critical points $T_c(L)$ found by PE are precisely these quasiwetting transitions, but for the particular case of critical wetting for $L = \infty$. Thus we are led to interpret PE’s $T_c(L)$ as a particular $T_w(L)$, and not as a shifted bulk critical point. Indeed, we propose the compelling interpretation of $T_w(L)$ being a shifted wetting transition. Consequently, we believe that the question of the bulk critical-point shift is still open. Where is the true $T_c(L)$? It is possible that the Landau theory, which neglects transverse fluctuations, misses this point altogether.

Indeed, beyond Landau theory, in the 3D Ising-model slab (of thickness $L$) with opposite surface fields, bulk two-phase coexistence is still possible well above the quasiwetting point $T_w(L)$. Coexistence then terminates at a quasi-2D critical point, $T_c(L)$, which bears no relation to wetting. For example, consider $L = 3$ layers (to begin with) and let the surface fields $H_1 = -H_2$ approach infinity in magnitude. In that case $T_w$ is pushed towards zero. At positive $T$ there are nevertheless two coexisting phases until a 2D-like critical point is reached. Similar critical points are expected for $L > 3$, at least for $L$ odd. We are presently investigating, by analytical methods and by simulations, how these critical points relate to the 3D roughening point or to the 3D bulk critical point, as $L \to \infty$. It remains challenging to ask if standard finite-size scaling still holds for the true $T_c(L)$.

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3. The critical point leap (at $L = \infty$) is complicated by the divergence of $\xi$ in the limit of large $L$, as seen from PE’s results for all temperatures from $T_w$ to $T_{c, \text{bulk}}$.
4. Details of our calculations, and global phase diagrams, will be published elsewhere.