Quasiwetting and Critical-Point Leaps

In a recent Letter, Parry and Evans¹ (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 $T_{c, bulk}$ 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.²

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/β_s} , where β_s 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 $T_{c, bulk} - T_c(L)$ 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 by PE converges to T_w and not to $T_{c, bulk}$ for $L \rightarrow \infty$ (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*³ 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 (novel) first-order, critical, and tricritical *quasiwetting*, respectively, for finite L^4 . The quasiwetting transitions,⁵ at $T_w(L)$, converge to the wetting transitions at T_w , for $L \rightarrow \infty$. 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 $L \rightarrow \infty$. It remains challenging to ask if standard finite-size scaling still holds for the true $T_c(L)$.

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¹A. O. Parry and R. Evans, Phys. Rev. Lett. 64, 439 (1990).

2F. Brochard-Wyart and P.-G. de Gennes, C,R. Acad. Sci. Paris, Ser. II 297, 223 (1983).

³The critical point leap (at $L = \infty$) is complicated by the divergence of ξ_{\parallel} in the limit of large L, as seen from PE's results for all temperatures from T_w to $T_{c, \text{bulk}}$.

4Details of our calculations, and global phase diagrams, will be published elsewhere.

 5 An experimental example of what we call quasiwetting is the stratification in thin 3 He- 4 He films. See J. P. Laheurte, J. C. Noiray, J. P. Ronagnan, and D. Sornette, J. Phys. (Paris) 47, 39 (1986); J. P. Romagnan, J. P. Laheurte, J. C. Noiray, and M. Papoular, Phys. Rev. B 37, 5639 (1988). For a Landau theory approach, see J. P. Desideri and D. Sornette, J. Phys. (Paris) 49, 1411 (1988).