Hyperscaling and nonclassical exponents for the line tension at wetting

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We study the effect of fluctuations on the line tension τ at first-order and continuous wetting transitions. We consider thermal wandering, strong fluctuations as in random media, and weak fluctuations as in quasiperiodic systems. We obtain $\alpha_l=\alpha_s+\nu_\parallel$, relating the exponent of τ, $2-\alpha_l$, to the surface specific-heat exponent α_s, and the interfacial correlation-length exponent $\nu_\parallel$. The singular behavior of τ at first-order wetting reveals that a critical phenomenon with a diverging correlation length, akin to complete wetting, is taking place.

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In this Brief Report, we are concerned with nonclassical critical phenomena associated with the contact line where three phases meet, near a wetting transition for the interfaces. Mean-field theory has predicted that, when the contact angle θ tends to zero, the line tension τ depends crucially on the order of the wetting transition. At first-order wetting, τ increases to a value $\tau_w>0$, or diverges. In contrast, at continuous (critical or multicritical) wetting, $\tau\to 0$, *from below* [1–5]. In general, τ was found to be *maximal* at wetting, and to show interesting singular behavior,

$$\tau_{\text{sing}}=\tau_\pm|t|^{2-\alpha_l}\ , \tag{1}$$

with $t\equiv(T-T_w)/T_w$, T_w the wetting temperature, τ_- (τ_+) applying to $t<0$ ($t>0$), and α_l the *line* specific-heat exponent. We recall $\theta\propto(-t)^{(2-\alpha_s)/2}$, with α_s the *surface* specific-heat exponent.

Experimentally, τ was found to play an important role in the nucleation of wetting layers [6]. A possible divergence of τ at first-order wetting, predicted for van der Waals forces [1,4], would lead to extraordinarily long lifetimes of metastable thick films [7]. Relaxation-time measurements could thus elucidate the form of the divergence of τ. Direct measurements of τ are difficult [8], but highly interesting, because the magnitude and sign of τ depend so strongly on the range of the intermolecular interactions, and on the character of the phase transition. Our approach differs much from previous studies of thermal capillary-wave fluctuations of the contact line [9]. We opt to focus on the *singular part* of τ and benefit from the availability of a fairly complete mean-field theory.

Mean-field results for τ at nth order (multi) critical wetting in systems with long-range forces were derived using the interface potential

$$V(l)=Al^{-(\sigma-1)}+Y_n l^{-(\sigma+n-2)}+E\ , \tag{2}$$

l being the interface displacement [4,5]. For van der Waals forces $\sigma=3$ (with retardation, $\sigma=4$). Furthermore, $n=2$ for critical, $n=3$ for tricritical [10], $n=4$ for fourth-order critical wetting [11]. On the other hand, for short-range forces,

$$V(l)=A\exp(-l)+Y_n\exp(-nl)+E\ . \tag{3}$$

We propose that the effect of fluctuations on the singular behavior of τ is described by the hyperscaling relation

$$2-\alpha_l=(d-2)\nu_\parallel\ , \tag{4}$$

where $\nu_\parallel$ is the critical exponent of the correlation length $\xi_\parallel$ parallel to the interface and d the dimensionality [12]. The mean-field results satisfy (4), provided we set $\nu_\parallel$ to its mean-field value and d to the upper critical dimension d_u. For thermal fluctuations $d_u=3-4/(\sigma+n)$ [12,5]. We expect (4) to hold in the nonclassical regime $d<d_u$, analogously to hyperscaling for the *surface* critical behavior at wetting [12].

Furthermore, we propose a more general scaling relation, valid also for nonthermal fluctuations, e.g., due to quenched random-field or random-bond disorder,

$$2-\alpha_l=\min\{\nu_\parallel-2\nu_\perp,(d-2)\nu_\parallel\}\ , \tag{5}$$

with $\nu_\perp$ the exponent of the correlation length $\xi_\perp$ perpendicular to the interface. The well-known roughness exponent ζ is defined by $\nu_\perp\equiv\zeta\nu_\parallel$.

If (5) is combined with the analogous relation for α_s [12], it gives the simple exponent equality

$$\alpha_l=\alpha_s+\nu_\parallel\ , \tag{6}$$

expected to be valid in all fluctuation regimes (and in mean field). We note that, at *bulk* criticality, $\alpha_l=\alpha_b+2\nu_b$ was derived for the *ordinary transition* [13].

As usual, (5) is derived heuristically from estimating the energy and entropy costs of line fluctuations, $\tau_{\text{F}}\propto L_\parallel\gamma_0(dl/dx)^2+k_BTL_\parallel^{2-d}\propto\gamma_0\xi_\perp^2\xi_\parallel^{-1}+k_BT\xi_\parallel^{2-d}$, where $L_\parallel$ is a length scale, and x a coordinate, parallel to the interface but perpendicular to the contact line, and γ_0 the interfacial tension [12]. We recall $\xi_\perp\propto t^{-\nu_\perp}$ and $\xi_\parallel\propto t^{-\nu_\parallel}$. For thermal fluctuations $\zeta=(3-d)/2$ ($1\le d\le 3$), so that (4) is recovered. Weaker than thermal fluctuations, with $\zeta<(3-d)/2$, will here be referred to as *subthermal*, to avoid confusion with the weak- and strong-fluctuation regimes discussed below. For subthermal fluctuations, hyperscaling (4) continues to

TABLE I. Exponents for nth-order multicritical wetting and long-range forces, for thermal or superthermal fluctuations. In the SF regime, $\nu_\parallel$ is not known explicitly, except in $d=2$.

Regime	Condition	Exponent $\nu_\parallel$	Exponent $2-\alpha_l$
MF	$\zeta<\zeta^\dagger\equiv 2/(\sigma+n)$	$(\sigma+n)/[2(n-1)]$	$(\sigma+n-4)/[2(n-1)]$
WF	$\zeta^\dagger\le\zeta<\zeta^*\equiv 2/(\sigma+1)$	$1/[2(1-\zeta/\zeta^*)]$	$(1-2\zeta)/[2(1-\zeta/\zeta^*)]$
SF	$\zeta\ge\zeta^*$	$\nu_\parallel$	$(1-2\zeta)\nu_\parallel$

hold, whereas for stronger than thermal fluctuations, here denoted by *superthermal,* with $\zeta>(3-d)/2$, we have $2-\alpha_l=\nu_\parallel-2\nu_\perp$. The heuristic scaling argument must be revised above d_u, as the leading term in τ is then $L_\parallel V(l_e)$, l_e being the equilibrium wetting layer thickness. The mean-field (MF) value for $2-\alpha_l$ is then recovered for $d\ge d_u$.

To a first approximation, the effect of fluctuations is incorporated by adding to $V(l)$ a term $l^{-\phi}$, with $\phi=\min\{2(1-\zeta)/\zeta,(d-1)/\zeta\}$, depending on whether the energy or entropy cost dominates in τ_F. An important preliminary remark is that the interface displacement model predicts that the amplitude τ_- in (1) *diverges* (as a function of the system size L) if the decay of $V(l)$ at large l is too slow. That is, for $\min\{\sigma-1,\phi\}\le 1$ [1,4]. For example, for $\sigma=2$ (relevant to nematic liquid crystals [14]), $\tau_-\propto\ln L$. Similar divergences occur in surface (for $\sigma\le 1$) and bulk (for $\sigma\le 0$) phenomena [4].

For thermal or superthermal fluctuations, a standard scaling analysis [12] leads to the results summarized in Table I for long-range forces and (multi) critical wetting in the weak- (WF) and strong- (SF) fluctuation regimes. The line tension exponent for van der Waals forces ($\sigma=3$) shows a high degree of universality, since $2-\alpha_l=\frac{1}{2}$ in both the MF and WF regimes, independent of n and the type (thermal or superthermal) of fluctuations. Note also that n is irrelevant in the WF regime.

The results for short-range forces in the MF and F regimes for thermal or superthermal fluctuations are presented in Table II. For the important case of thermal fluctuations and critical wetting ($n=2$) in $d=d_u=3$ it follows that $2-\alpha_l=\nu_\parallel$, which is known to be a nonuniversal exponent, varying between 1 and ∞ as a function of a capillary-wave parameter [12]. However, critical-wetting theory in $d=3$ is currently being refined [15]. For $d=2$, we find $2-\alpha_l=0$. Since logarithmic corrections may be present, this result gives no clue as to whether τ vanishes, remains finite, or diverges at wetting. An exact calculation of the *point* tension (since the line is zero dimensional) near critical wetting ($n=2$) in the $2d$ Ising model [16] appears indispensable. Note that the nonclassical prediction is quite different from the MF result $2-\alpha_l=1$.

TABLE II. Exponents for nth-order multicritical wetting and short-range forces, for thermal or superthermal fluctuations. In the MF regime $2-\alpha_l=\nu_\parallel$.

Regime	Condition	$2-\alpha_l$
MF	$d>d_u$ $(\zeta=0)$	$n/[2(n-1)]$
F	$d\le d_u$ $(\zeta\ge 0)$	$(1-2\zeta)\nu_\parallel$

There is a lot of interest in systems with short-range forces and superthermal fluctuations [12]. For quenched random-field disorder, $\zeta=(5-d)/3$ (for $2\le d\le 5$). Thus, for $d=3$, $2-\alpha_l=-\nu_\parallel/3$, suggesting that τ diverges for $t\to 0$. However, since $\zeta=\frac{2}{3}$ and thus $\phi=1$, the amplitude τ_- is expected to diverge as $\ln L$. For random-bond disorder ζ is less well known. Since probably $\zeta=0.45\pm0.05$ in $d=3$ [12,17], τ possibly vanishes for $t\to 0$, since $2-\alpha_l\approx 0.1\nu_\parallel$. In $d=2$ (and for $\zeta\ge\frac{1}{2}$), $\nu_\parallel=1/(1-\zeta)$ is known exactly, and we find $2-\alpha_l=(1-2\zeta)/(1-\zeta)$, for the point tension. Since $\zeta\ge\frac{2}{3}$ for both random fields and random bonds, τ_- should diverge (with L) already at $t<0$.

There is also much interest in subthermal fluctuations, relevant to interfaces in aperiodic or quasiperiodic systems, like quasicrystals [18,19]. There, ζ is temperature dependent and thus highly nonuniversal. For long-range forces and (multi) critical wetting we find $2-\alpha_l=(d-2)\nu_\parallel$, for $\zeta\ge\zeta^\dagger\equiv(d-1)/(\sigma+n-2)$. A WF regime is defined by $\zeta^\dagger\le\zeta<\zeta^*\equiv(d-1)/(\sigma-1)$ and we obtain $\nu_\parallel=1/[d-1-\zeta(\sigma-1)]$, in agreement with an earlier result for $d=2$ [19]. In the SF regime, $\zeta\ge\zeta^*$, a finite value $\nu_\parallel=1/(1-\zeta)$ was obtained in $d=2$ (and $\zeta<\frac{1}{2}$) [19], which we note to be formally the same as for $\zeta\ge\frac{1}{2}$. We conclude $2-\alpha_l=0$ in $d=2$(WF and SF). For short-range forces, we obtain $d_u=3$, as for thermal wandering. In the F regime ($d<3$), we find $2-\alpha_l=(d-2)\nu_\parallel$.

Next we turn to the experimentally more accessible case of first-order wetting (for which $2-\alpha_s=1$). Explicit mean-field results indicate that we may expect $\tau=\tau_w>0$ or $\tau=+\infty$ at wetting [1–4]. We write

$$\tau=\tau_w+\delta\tau\ , \tag{7}$$

where $\delta\tau$ contains the singular part,

$$\delta\tau=\tau_-(-t)^{2-\alpha_l}\ . \tag{8}$$

A first-order wetting transition is generally expected to possess a prewetting extension into the bulk one-phase region. The thin and (finitely) thick wetting layers coexisting at prewetting meet at a boundary line, with *boundary tension* [20]

$$\hat{\tau}=\tau_w+\delta\hat{\tau}\ , \tag{9}$$

and, near wetting,

$$\delta\hat{\tau}=\hat{\tau}_+h^{2-\hat{\alpha}_l}=\tau_+t^{2-\alpha_l'}\ , \tag{10}$$

TABLE III. Exponents for first-order wetting and long-range forces, for thermal or superthermal fluctuations.

Regime	Condition	Exponent Δ	$\hat{\nu}_{\parallel}$	$2-\hat{\alpha}_l$
MF	$\zeta<\zeta^{\dagger}\equiv 2/(\sigma+1)$	$\sigma/(\sigma-1)$	$(\sigma+1)/(2\sigma)$	$(\sigma-3)/(2\sigma)$
F	$\zeta\geq\zeta^{\dagger}$	$(2-\zeta)/[2(1-\zeta)]$	$1/(2-\zeta)$	$(1-2\zeta)/(2-\zeta)$

where the field $h\,(>0)$ measures the deviation from bulk two-phase coexistence. Note that τ_w, if it exists, takes the same value in (7) and (9), and that $\hat{\tau}\geq 0$ [20,4].

Mean-field theory [4] predicts, for long-range forces,

$$2-\alpha_l=\begin{cases}(\sigma-3)/[2(\sigma-1)] & \text{for } \sigma>3 \text{ or } 2<\sigma<3\\ 0(\log) & \text{for } \sigma=3\ ,\end{cases} \tag{11}$$

where 0(log) means exponent zero but logarithmic divergence. It was found that τ diverges at wetting for $2<\sigma\leq 3$. Again, for $\sigma\leq 2$, τ_- diverges as a function of L, already for $t<0$. We note that the same exponents apply to the line tension of the unstable critical droplet in the nucleation process at complete wetting $(t>0)$ [21]. Along prewetting and for $h\to 0$ [4],

$$2-\hat{\alpha}_l=\begin{cases}(\sigma-3)/(2\sigma) & \text{for } \sigma>3 \text{ or } 1<\sigma<3\\ 0(\log) & \text{for } \sigma=3\ .\end{cases} \tag{12}$$

It was found that $\hat{\tau}$ diverges at wetting for $\sigma\leq 3$. For short-range forces, mean-field theory [4] predicts $\delta\tau\propto(-t)^{1/2}\ln(-t)$, and $\delta\hat{\tau}\propto h^{1/2}$, so that

$$2-\alpha_l=2-\hat{\alpha}_l=\tfrac{1}{2}\ . \tag{13}$$

We observe that

$$2-\alpha_l=2-\alpha_l'=\Delta(2-\hat{\alpha}_l)\ , \tag{14}$$

where Δ is the usual crossover exponent describing the tangential approach of the prewetting line towards the bulk coexistence curve, near T_w [12,22]. We thus expect standard scaling,

$$\delta\tau=|t|^{2-\alpha_l}\Phi(t/h^{1/\Delta})\ . \tag{15}$$

Interestingly, (5) (at $d=d_u$) and (6) hold for the mean-field exponents at *first-order* wetting. The relevant correlation lengths are those that diverge approaching *complete wetting*, for $h\to 0$ [23]. We recall $\xi_{\parallel}\propto h^{-\hat{\nu}_{\parallel}}$ and $\xi_{\perp}\propto h^{-\hat{\nu}_{\perp}}$, with $\hat{\nu}_{\perp}=\zeta\hat{\nu}_{\parallel}$. We now propose that (5) holds as a scaling relation in the nonclassical regime $d<d_u$. Strikingly, the singular behavior of the line tension at a *first-order* wetting transition reveals that a *critical* phenomenon (with a diverging correlation length) is taking place. This critical phenomenon is closely related to that known to occur at complete wetting [23].

Considering thermal or superthermal fluctuations, we obtain the results for long-range forces summarized in Table III. These field-related exponents describe the approach of T_w along prewetting, for $t(>0)\to 0$ and $h(>0)\to 0$. The thermal exponents, associated with the approach of T_w from partial wetting along bulk coexistence, for $h=0$ and $t(<0)\to 0$, are found by multiplying those in Table III by Δ, in accordance with (15). For short-range forces, in the MF regime, for $d>d_u$ (and $\zeta=0$), we have $\Delta=1$ and $2-\alpha_l=\nu_{\parallel}=\frac{1}{2}$. In the F regime, for $d\leq d_u$ (and $\zeta\geq 0$), the exponents are the same as in Table III (F).

Finally we turn to subthermal fluctuations. For long-range forces, we find $2-\alpha_l=(d-2)\nu_{\parallel}=(d-2)/(d-1)$ in the F regime, for $\zeta>\zeta^{\dagger}\equiv(d-1)/(\sigma-1)$. Furthermore, we obtain $\Delta=(d-1+\zeta)/(d-1)$, so that $2-\hat{\alpha}_l$ follows from (14). For short-range forces, we find $d_u=3$, as for thermal fluctuations. The exponents in the F regime $(d<3)$ are the same as in the F regime for long-range forces.

We propose the following conclusions. (i) The effect of fluctuations on the singular part of the line tension at wetting is contained in the standard interfacial correlations. The exponent $2-\alpha_l$ is related by hyperscaling (for thermal and subthermal fluctuations), and by different scaling (for superthermal fluctuations), to the interface correlation-length exponents. The exponent equality $\alpha_l=\alpha_s+\nu_{\parallel}$ is generally valid. (ii) This suggests new experimental routes, e.g., in systems with thermal or superthermal fluctuations, from measuring $\tau-\tau_w$ to estimating $\nu_{\parallel}-2\nu_{\perp}$. Combined with contact-angle measurements, giving $2-\alpha_s$ and thus $2(\nu_{\parallel}-\nu_{\perp})$, *both* correlation-length exponents can be determined. Alternatively, in general, a line tension measurement combined with a contact-angle determination give $\nu_{\parallel}$, using (6). On the other hand, a measurement of the wetting layer thickness l_e allows one to estimate $\nu_{\perp}$ [12]. (iii) The global behavior of τ at wetting (vanishing, finite, or diverging) depends on the regular background τ_w, the amplitude τ_-, and the exponent $2-\alpha_l$. Possible logarithmic corrections turn out to be crucial (as exemplified by the mean-field results) and the amplitude τ_- may diverge in the thermodynamic limit $(L\to\infty)$.

In a future publication we will discuss the universality of the *line amplitude ratio* $R_{+-}\equiv\tau_+/\tau_-$ at first-order wetting. Briefly, we propose an analogy between first-order wetting and *interface* critical end points. Partial wetting, complete wetting, and prewetting correspond to three-*interface* coexistence, interface criticality, and two-interface coexistence, respectively. An analysis of τ in the form (7) then runs parallel to that of the interfacial tension near bulk critical end points, leading to universal amplitude ratios [24], of current experimental interest [25].

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