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LETTER TO THE EDITOR

Absence of a stiffness instability for a model critical-wetting transition in three dimensions

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Abstract. We have tested the generality of the stiffness instability mechanism recently proposed by Fisher and Jin for the critical wetting phase transition in three-dimensional systems with short-ranged forces. We extend the analysis of Fisher and Jin to a class of Aukrust–Hauge type models and find that the stiffness instability is specific to the case where the unrenormalized transition is precisely second order (i.e where the mean-field specific heat critical exponent is precisely zero). A linear functional renormalization-group analysis of this Aukrust–Hauge class of models yields exactly the same dramatic fluctuation-induced non-universal critical exponents that have previously been predicted. We conclude by considering possible implications of this result on future Ising model simulations and on the basis of this propose a numerical test for the validity of existing renormalization-group analyses of continuum effective interfacial Hamiltonians.

Over recent years much attention has been focused on the nature of the critical-wetting phase transition in three-dimensional systems with short-ranged forces [1–11]. Recall that the initial renormalization group (RG) predictions [1–3] of dramatic non-universal critical exponents have not been observed in extensive Monte Carlo simulation studies of the Ising model [4–7]. More recently Fisher and Jin [8, 9] have argued that for the Landau–Ginzburg–Wilson (LGW) Hamiltonian with strictly short-ranged surface interactions a stiffness instability mechanism exists which may drive a bare critical-wetting transition fluctuation-induced weakly first-order. The origins of this mechanism are found in the inclusion of a specific position dependent stiffness coefficient in the effective interfacial Hamiltonian model [10–13]. In the present letter we test the robustness of the instability mechanism by studying renormalization effects for a different model of wetting in three dimensions with short-ranged forces. We shall show that within the class of models studied the instability mechanism is specific to the case where the bare, mean-field (MF), critical-wetting transition is precisely second order in the Ehernfest classification (i.e $\alpha_S^{MF} = 0$). For the cases where the unrenormalized models result in critical-wetting with mean-field specific heat critical exponent $\alpha_S^{MF} < 0$ the linear functional renormalization group analysis (with the appropriate position dependent stiffness coefficient) yields the same fluctuation-induced non-universal critical exponents that have previously been predicted using cruder models.

The starting point for our analysis is a microscopic model Hamiltonian in the form of the local-density-approximation (LDA) functional [14]

$$H_{\rm LDA}[\rho(\boldsymbol{r})] = \int {\rm d}\boldsymbol{r}\, f_h[\rho(\boldsymbol{r})] + \frac{1}{2}\int\int {\rm d}\boldsymbol{r}_1\, {\rm d}\boldsymbol{r}_2 \omega(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) + \int {\rm d}\boldsymbol{r}\rho(\boldsymbol{r})(V(\boldsymbol{r}) - \mu) \tag{1}$$

where $f_h(\rho)$ is the bulk free-energy density of hard spheres. We introduce a simple Yukawa form for the attractive fluid–fluid interaction $\omega(r)$

$$\omega(r) = -\frac{\alpha\lambda^3 e^{-\lambda r}}{4\pi\lambda r} \tag{2}$$

where $\alpha = -\int dr\omega(r)$ is the integrated strength and λ^{-1} is the decay length. We consider a planar system $V(r) \equiv V(z)$, where the wall-fluid external field is

$$V(z) = \begin{cases} -\epsilon e^{-\lambda\lambda_v z} & ; z > 0 \\ \infty & ; z < 0 \end{cases} \tag{3}$$

with $\epsilon > 0$. The parameter μ corresponds to a chemical potential. At mean-field level where fluctuations may be ignored $H_{\mathrm{LDA}}[\rho(r)]$ may be identified with the grand-potential density functional which must be minimized to yield the MF (planar) density distribution $\breve{\rho}(z)$. Consequently for this case the model reduces to the mean-field analyses of Sullivan [15] and Aukrust–Hauge [16] for the regimes $\lambda_v = 1$ and $\lambda_v \neq 1$ respectively. Let us suppose that the wall–gas interface at chemical potential $\mu = \mu_{\mathrm{sat}}(T)^-$ is critically wet by liquid as $T \to T_W^-(\epsilon, \lambda_v)$ for some range of parameters ϵ and λ_v. Note that λ can be set equal to unity without loss of generality. For the Sullivan model ($\lambda_v = 1$) a critical-wetting transition occurs when $\alpha\rho_l(T) = 2\epsilon$, where $\rho_l(T)$ is the bulk density of the liquid phase at temperature T, and one finds that the mean-field critical-wetting exponents for the surface specific heat, adsorption and transverse correlation length are $\alpha_S^{\mathrm{MF}} = 0$, $\beta_S^{\mathrm{MF}} = 0(\ln)$ and $\nu_\parallel^{\mathrm{MF}} = 1$ respectively. For the Aukrust–Hauge model a critical wetting transition only occurs for $\lambda_v \geqslant 1$ and temperatures such that $\kappa_l < \lambda_v$, where κ_l is the dimensionless inverse bulk liquid (true) correlation length measured in units of λ. The values of the corresponding critical exponents are the same as those of the Sullivan model if $\lambda_v > 2\kappa_l$. However, if λ_v lies in the range $\kappa_l < \lambda_v < 2\kappa_l$ then the mean-field critical exponents take on the non-universal values [16] $\alpha_S = -(2\kappa_l - \lambda_v)/(\lambda_v - \kappa_l)$, $\beta_S = 0(\ln)$ and $\nu_\parallel = \lambda_v/2(\lambda_v - \kappa_l)$.

In this letter we seek to understand the effect of renormalization in these models for dimension $d = 3$ by deriving an effective-interfacial Hamiltonian $H_I[l(y)]$ which has the form

$$H_I[l(y)] = \int dy \left\{ \frac{\Sigma(l; T, \mu, \epsilon, \lambda_v)}{2} (\nabla l(y))^2 + W(l; T, \mu, \epsilon, \lambda_v) \right\} \tag{4}$$

where $\Sigma(l; T, \mu, \epsilon, \lambda_v)$ is the position dependent stiffness coefficient and $W(l; T, \mu, \epsilon, \lambda_v)$ is the binding potential. Following the work of Fisher and Jin we shall adopt the *crossing-criterion* definition of the collective coordinate $l(y)$, where y is the transverse displacement vector along the wall. Consequently, $l(y)$ defines a surface of fixed density ρ^X so that $\rho(z = l(y), y) = \rho^X \; \forall y$. The value of ρ^X is chosen to lie in the interval $\rho^X \in (\rho_g(T), \rho_l(T))$ but need not be specified further. The effective Hamiltonian is defined by tracing over density distributions that respect the crossing-criterion and then using a saddle-point approximation to evaluate the partial trace. The result is the Fisher–Jin identification

$$H_I[l(y)] = H_{\mathrm{LDA}}[\rho_\Xi(r; l(\cdot))] \tag{5}$$

where $\rho_\Xi(r; l(\cdot))$ is the profile that minimizes (1) subject to the crossing-criterion. Performing the minimization of (1) yields

$$0 = \mu_h(\rho_\Xi(r; l(\cdot))) - \mu + V(r) + \int_0^\infty dr_1 \omega(|r - r_1|)\rho_\Xi(r_1; l(\cdot)) \tag{6}$$

where $\mu_h(\rho)$ is the chemical potential for a homogeneous system of hard spheres of density ρ. In addition we need to impose two boundary conditions on $\rho_\Xi(\boldsymbol{r}; l(\cdot))$. Firstly a bulk condition (A)

$$\lim_{z\to\infty} \rho_\Xi(\boldsymbol{r}; l(\cdot)) = \rho_b(T, \mu) \tag{7}$$

where ρ_b is the equilibrium bulk density; and secondly a natural continuity condition arising from the crossing-criterion (B)

$$\rho_\Xi(\boldsymbol{r} = (l(y)^\pm, y); l(\cdot)) = \rho^X. \tag{8}$$

We shall show that knowledge of the planar constrained profile $\rho_\pi(z; l)$, which satisfies (6), (7) and (8) for the case $l(y) \equiv l$, suffices to determine $W(l; T, \mu, \epsilon, \lambda_v)$ and $\Sigma(l; T, \mu, \epsilon, \lambda_v)$ exactly. To demonstrate this we first note that it is easier to consider the field $\mu_h^\pi(z; l) \equiv \mu_h(\rho_\pi(z; l))$, a monotonically increasing function of $\rho_\pi(z; l)$, as our order parameter. For the choice of potentials (2) and (3) it is straightforward to show that the integral equation (6) can be converted to a second-order differential equation for μ_h^π

$$\frac{\partial^2 \mu_h^\pi(z; l)}{\partial z^2} = \mu_h^\pi(z; l) - \mu - \alpha\rho_\pi(z; l) - \epsilon(1 - \lambda_v^2)\mathrm{e}^{-\lambda_v z} \tag{9}$$

with the boundary condition at the wall

$$\left(\frac{\partial \mu_h^\pi(z; l)}{\partial z}\right)_{z=0^+} = \mu_h^\pi(0^+; l) - \mu - \epsilon(1 + \lambda_v) \tag{10}$$

and recall we have set $\lambda = 1$. It is convenient to define the function

$$\psi(\mu_h^\pi) \equiv (\mu_h^\pi - \mu)^2 - 2\alpha(p_h(\rho_\pi(z; l)) - p) \tag{11}$$

with $p_h(\rho)$ the bulk hard sphere pressure. The function $\psi(\mu_h^\pi)$ plays the role of the usual double-well potential from field-theory.

Within our theory the binding potential $W(l; T, \mu, \epsilon, \lambda_v)$ is defined (up to l-independent terms) by

$$W(l; T, \mu, \epsilon, \lambda_v) = \frac{H_{\mathrm{LDA}}[\rho_\pi(z; l)] + pV}{A} \tag{12}$$

where p is the bulk pressure and V and A are the semi-infinite volume and transverse area respectively. After a little algebra it is possible to express $W(l; T, \mu, \epsilon, \lambda_v)$ elegantly in terms of the field $\mu_h^\pi(z; l)$. We find

$$W(l; T, \mu, \epsilon, \lambda_v) = \frac{1}{2\alpha}\int_0^\infty \mathrm{d}z \left\{\left(\frac{\partial \mu_h^\pi}{\partial z}\right)^2 + \psi(\mu_h^\pi) + 2\epsilon(\lambda_v^2 - 1)\mu_h^\pi \mathrm{e}^{-\lambda_v z}\right\} + \frac{1}{2\alpha}\left[2\mu_h^\pi\left(\frac{\partial \mu_h^\pi}{\partial z}\right) - (\mu_h^\pi)^2\right]_{z=0^+} \tag{13}$$

where we have omitted l-independent terms that depend only on $V(z)$.

The stiffness coefficient $\Sigma(l; T, \mu, \epsilon, \lambda_v)$ is evaluated following the argument of Fisher, Jin and Parry [17]. Consider the ansatz

$$\rho_\Xi(\boldsymbol{r}; l(\cdot)) \approx \rho_\pi(z; l(\boldsymbol{y})) \qquad \boldsymbol{r} = (z, \boldsymbol{y}). \tag{14}$$

Substitution of this trial function shows that (6) is indeed solved up to terms of $\mathcal{O}(|\boldsymbol{\kappa}_\perp|^2)$ where $\boldsymbol{\kappa}_\perp$ is a parallel (i.e along the wall) wavevector. Moreover the approximation (14) automatically satisfies the required boundary conditions A and B. It follows that the ansatz suffices to exactly determine the Hamiltonian (4) to order $|\boldsymbol{\kappa}_\perp|^2$. In this way we derive the following 'Triezenberg–Zwanzig' type expression for $\Sigma(l; T, \mu, \epsilon, \lambda_v)$

$$\Sigma(l; T, \mu, \epsilon, \lambda_v) = \frac{1}{\beta}\int_0^\infty \int_0^\infty \mathrm{d}z_1\, \mathrm{d}z_2 \frac{\partial \rho_\pi(z_1; l)}{\partial l} C_2^{\mathrm{MF}}(z_1, z_2) \frac{\partial \rho_\pi(z_2; l)}{\partial l} \tag{15}$$

where the function $C_2^{\mathrm{MF}}(z_1, z_2)$ is the mean-field result for the second-moment of the direct correlation function [18]

$$C_2^{\mathrm{MF}}(z_1, z_2) = \frac{\alpha\beta}{4}(1 + |z_1 - z_2|)\mathrm{e}^{-|z_1 - z_2|}. \tag{16}$$

It is possible to convert the expression (15) into a simpler one involving the field $\mu_h^\pi(z; l)$. We only quote our final result

$$\Sigma(l; T, \mu, \epsilon, \lambda_v) = \frac{1}{\alpha}\int_0^\infty \mathrm{d}z \left(\frac{\partial \mu_h^\pi(z; l)}{\partial l}\right)^2. \tag{17}$$

The proof of this result is similar to the analysis given in the appendix of Parry and Evans [18]. Equations (9), (10), (13) and (17) appropriate to the LDA model (1) may now be studied in precisely the same way as Fisher and Jin analysed the corresponding Landau–Ginzburg–Wilson equations. We choose a double-parabola form for the function $\psi(\mu_h^\pi)$. Our results are as follows.

Specific heat exponent $\alpha_{\mathrm{S}}^{\mathrm{MF}} = 0$. Such an exponent arises for the cases $\lambda_v = 1$ (Sullivan-type) and $\lambda_v > 2\kappa_l$, $\lambda_v > 1$. The case $\lambda_v = 1$ is particularly straightforward since it is almost identical in structure to the Fisher–Jin analysis. We find that the leading two terms in the expansions of $W(l; T, \mu, \epsilon, \lambda_v)$ and $\Sigma(l; T, \mu, \epsilon, \lambda_v)$, at coexistence $\mu = \mu_{\mathrm{sat}}(T)^-$, are the same as for the LGW model. It follows that provided the value of $\omega \equiv \kappa_l^2 k_{\mathrm{B}} T / 4\pi \Sigma_{lg}$ is not too large, the transition is driven fluctuation-induced first-order. Here Σ_{lg} is the surface tension of the liquid-gas interface at temperature T.

Specific heat exponent $\alpha_{\mathrm{S}}^{\mathrm{MF}} < 0$. A negative specific heat critical exponent arises for the case $2\kappa_l > \lambda_v > \kappa_l$, $\lambda_v > 1$ where our results for the expansions of $W(l; T, \mu, \epsilon, \lambda_v)$ and $\Sigma(l; T, \mu, \epsilon, \lambda_v)$, at saturation chemical potential, are

$$W(l; T, \mu, \epsilon, \lambda_v) = \omega_\kappa \mathrm{e}^{-\kappa_l l} + \omega_\lambda \mathrm{e}^{-\lambda_v l} + \mathcal{O}(\mathrm{e}^{-2\kappa_l l}) \tag{18}$$

and

$$\Sigma(l; T, \mu, \epsilon, \lambda_v) = \Sigma_{lg} + s_\kappa \mathrm{e}^{-\kappa_l l} + s_\lambda \mathrm{e}^{-\lambda_v l} + \mathcal{O}(l\mathrm{e}^{-2\kappa_l l}). \tag{19}$$

The coefficients ω_κ and s_κ are both proportional to the reduced temperature $\tau \equiv (T - T_{\mathrm{W}}^{\mathrm{MF}})/T_{\mathrm{W}}^{\mathrm{MF}}$ whilst ω_λ and s_λ are non-zero and positive in the vicinity of $\tau = 0$. Consequently we observe that there is no longer a negative next-to leading order term in the stiffness coefficient to drive the transition first-order, hence if we apply the renormalization group scheme of Fisher and Jin it follows that the transition remains second-order. The values of the critical exponents are the same as those calculated by Hauge and Olaussen [19]. For the correlation length exponent the RG results are

$$\nu_{\parallel} = \begin{cases} \dfrac{\lambda_v}{2(\lambda_v - \kappa_l)} \dfrac{1}{(1 - \frac{\lambda_v}{2\kappa_l}\omega)} & ; 0 < \omega < \omega_c \\ (\sqrt{2} - \sqrt{\omega})^{-2} & ; \omega_c < \omega < 2 \\ \infty & ; \omega > 2 \end{cases} \tag{20}$$

where

$$\omega_c = 2\left(\frac{\kappa_l}{\lambda_v}\right)^2 . \tag{21}$$

Our results show that the stiffness instability is specific to the case where the mean-field (bare) critical wetting transition is strictly second order ($\alpha_S^{MF} = 0$). For the case $\alpha_S^{MF} < 0$ there is no stiffness instability and the critical wetting transition is characterized by non-universal (and non-MF) critical exponents.

Finally we discuss possible implications of these findings on the interpretation of Ising model simulations. One way of testing the stiffness instability mechanism proposed by Fisher and Jin would be to simulate a model with enough tunable parameters that both critical and fluctuation-induced first-order wetting transitions are possible. To this end we first note that the phase diagram of the LDA model (1) is the same as that of the modified LGW Hamiltonian

$$H[m(r)] = \int dr \left\{ \frac{K}{2}(\nabla m(r))^2 + \Phi(m(r)) + \delta(z)\Phi_1(m(r)) + \bar{\epsilon}_1 e^{-\lambda z} m(r) \right\} \tag{22}$$

where $\Phi(m)$ and $\Phi_1(m)$ are standard bulk and surface energy-density functions. Analysis of this model shows that for the choice of repulsive surface interaction $\bar{\epsilon}_1 > 0$ and an attractive surface field h_1 the bare critical wetting transition remains second-order after renormalization provided $\kappa < \lambda < 2\kappa$ where κ is the inverse bulk correlation length of the adsorbed phase. Next we note that (22) may be regarded as the continuum limit of a semi-infinite Ising model with attractive surface field and an additional repulsive term $\propto e^{-\lambda z}$ which acts on spins away from the surface. A computer study of this lattice Hamiltonian would therefore provide a straight test of the proposed stiffness instability mechanism. For example, if the simulations of this model revealed the appropriate non-universal fluctuation-induced critical exponents we should conclude that theory and simulation are in good agreement. If this were the case, the stiffness instability mechanism of Fisher and Jin would almost certainly be the correct interpretation of the original Ising model simulation results. If on the other hand the simulations of this model did not reveal dramatic non-universal and non-MF critical exponents we would have to conclude that the existing RG analyses of continuum effective Hamiltonians do not describe some essential physics associated with the phase transition in a three-dimensional lattice model.

In conclusion we have shown that for a model *critical*-wetting transition with short-ranged forces in three-dimensions the Fisher–Jin stiffness instability is specific to the case where the unrenormalized phase transition is precisely second-order. Renormalization group analysis of an 'Aukrust–Hauge' type model still predicts dramatic fluctuation-induced non-universal critical exponents.

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