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Universal fluctuation-induced corrections to the Kelvin equation for capillary condensation

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Abstract. Interfacial fluctuations in complete wetting films give rise to important corrections to the macroscopic Kelvin equation for the location of the shifted first-order (condensation) transition that occurs when a fluid (or an Ising magnet) is confined between two parallel adsorbing walls. The wall separation L that enters the usual Kelvin equation must be replaced by $L - \phi l(\mu^*)$, where l is the thickness of the wetting film at the chemical potential μ^* at which capillary condensation occurs and ϕ is an amplitude. For pure systems with short-ranged forces thermal wandering is insufficient to renormalize the simple geometric result $\phi = 2$ for bulk dimensions $d \geq 3$. However, in $d = 2$, where fluctuations are much stronger, we predict $\phi = 3$ throughout the weak fluctuation regime of complete wetting which includes long-ranged dispersion forces as well as short-ranged forces. Our prediction is supported by an explicit analysis of a $d = 2$ interfacial Hamiltonian. This shows that pseudo-phase coexistence, characterized by an exponentially large transverse correlation length, occurs for an exponentially narrow range of μ^* determined by the corrected Kelvin equation with $\phi = 3$. We also speculate that interfacial wandering in quenched random media should lead to equivalent corrections to the Kelvin result, but with amplitude $\phi = (2 - \zeta)/(1 - \zeta)$, where ζ is the interface wandering exponent, in the fluctuation dominated regime.

1. Introduction

When studying the effects of confinement or finite-size on the phase equilibria of a fluid, or an Ising magnet, two fundamental questions are (i) what is the extent and character of the shift of any phase transition (relative to the values of the thermodynamic fields which locate the transition in bulk)? and (ii) what is the extent of the rounding of the transition? Phenomenological finite-size scaling theory, reviewed in [1–4], answers these questions successfully for critical transitions and makes a number of predictions for universal critical amplitudes associated with (fluctuation-dominated) finite-size effects [5]. Ideas of conformal invariance have been especially useful in understanding this universality [6]. The subject of finite-scaling for first-order phase transitions is somewhat less extensive [7] and theorists have usually focused on the determination of the length scales which control the rounding of the transition in confining geometries that suppress true symmetry breaking and phase coexistence [7–12]. Such work is complemented by a large (mainly physical chemistry) literature concerned with the shift of the bulk liquid–gas (condensation) transition when a fluid is confined in parallel plate (slit) or cylindrical geometries. If the confining substrates (walls) favour liquid, capillary condensation occurs at bulk gas pressures p that lie below the bulk saturated gas pressure $p_{\text{sat}}(T)$ for the given temperature T . This

phenomenon is important in experimental investigations of the adsorption of gases on mesoporous solids and theoretical treatments can be traced back to Zsigmondy [13], who invoked the macroscopic Kelvin [14] equation for the change in vapour pressure due to a curved meniscus, to interpret adsorption data. In recent years many detailed mean-field density functional theories and computer simulations have been performed to determine the location and nature of phase transitions of simple fluids confined in model pores; for a brief review see [15]. Such studies have shown that the simple (Kelvin) prediction for the shift in chemical potential

$$\mu^* - \mu_{\text{sat}} = -2\sigma_{\text{lg}} \cos \theta / L(\rho_{\text{l}} - \rho_{\text{g}}) \quad L \rightarrow \infty \quad (1)$$

at which two-phase coexistence occurs in finite geometry remains accurate for wall separations L (or cylinder radii R_{c}) as small as 10 molecular diameters—provided the walls are only partially wet by liquid, i.e. the contact angle $\theta > 0$. Note that σ_{lg} is the surface tension of the planar liquid–gas interface. When $\theta = 0$, so that complete wetting occurs, the presence of thick adsorbed (wetting) films can lead to important corrections to the Kelvin equation (1). These were described first in a pioneering paper of Derjaguin [16] but they have been re-derived using density functional theory [17, 18] and have been sought for in Monte Carlo simulations of a lattice gas model [19]. Such corrections were obtained at the mean-field level, i.e. there was no attempt to incorporate fluctuation contributions.

In the present paper we reconsider the shift of the liquid–gas (spin up–spin down) coexistence curve for a fluid (Ising magnet) confined in slit-geometry concentrating on the case where the identical adsorbing walls are completely wet by liquid (spin up), say, when the bulk phase is a gas (spin down) at $\mu = \mu_{\text{sat}}^-$ and $L = \infty$. We argue that the location of the shifted bulk transition is given, for large L , by (1) with $\theta = 0$ and the wall separation L replaced by $L - \phi l$, where l is the thickness of a wetting film and ϕ is an amplitude which, in general, depends on the nature of wall–fluid and fluid–fluid forces as well as the interfacial wandering of the thick wetting films adsorbed at the walls. In bulk dimension $d = 2$, within the weak fluctuation regime of complete wetting, which incorporates long-ranged dispersion forces as well as short-ranged forces, we predict that ϕ takes the universal value 3. We compare this result with the corresponding predictions for $d = 3$ where mean-field treatments should remain valid and ϕ should be dependent on the range of the wall–fluid and fluid–fluid forces [16–18]. The results of an explicit calculation, based on an effective interfacial Hamiltonian, confirm our prediction for $d = 2$. Finally we speculate that equivalent corrections to the Kelvin equation should apply for quenched random media. Since the amplitude ϕ is directly related to the interface wandering exponent ζ we contrast the values of ϕ obtained from thermal wandering in a pure fluid with those from interfacial wandering in systems with random bonds or with random fields.

2. Heuristic treatments

We begin by recalling the derivation of (1); further details may be found in [17, 18]. For large wall separations L the confined fluid will exhibit true phase coexistence (at a fixed temperature below the shifted bulk critical temperature $T_{\text{c},L}$) along a line of points in (μ, L) space—provided the bulk dimension $d \geq 3$. Here μ is the chemical potential of the (bulk) reservoir. For $d = 2$, below a pseudo-critical temperature, we expect to find pseudo-phase coexistence in the confined fluid (or near spontaneous

symmetry breaking for an Ising strip) characterized by an exponentially large transverse correlation length $\xi_{\parallel} \sim L^{1/2} \exp L$ [9, 20, 21] which measures the distance between domain walls. Each domain will be described by a liquid-like or gas-like density profile. Pseudo-coexistence should be restricted to a very narrow range of values of μ , i.e. the rounding of the transition is expected to be exponentially small $\sim k_B T / (\rho_l - \rho_g) \xi_{\parallel} L \sim L^{-3/2} \exp(-L)$ [9, 21]. It is the location $\mu^* - \mu_{\text{sat}}$ of this rounded transition we shall be concerned with here. Consider first the case where the contact angle (defined, as usual, for a single wall and $\mu = \mu_{\text{sat}}$) satisfies $0 < \theta < \pi/2$ so that the identical walls exert surface fields which favour liquid but are not completely wet. Phase coexistence or pseudo-coexistence will then occur on the 'gas side' of bulk coexistence, i.e. at $\mu < \mu_{\text{sat}}(T)$. For large L we can view the coexisting phases in the slit as a dilute 'gas' (g) at a pressure $p(\mu, T)$ that is fixed by the reservoir and a condensed 'liquid' (l) at a pressure p^\dagger that is equal to that of a metastable bulk liquid at the given (μ, T) [17, 18]. Then the total grand potential per unit area, or unit length in $d=2$, of the two phases can be approximated by

$$\frac{\Omega_g}{A} \approx -pL + 2\sigma_{wg} \quad (2a)$$

and

$$\frac{\Omega_l}{A} \approx -p^\dagger L + 2\sigma_{wl} \quad (2b)$$

where σ_{wg} and σ_{wl} refer to the single wall ($L = \infty$) wall-gas and wall-liquid interfacial tensions, respectively. Implicit in this treatment is the assumption that the density profiles of the two phases are almost constant throughout the volume of the slit: $\rho(r) \approx \rho_g$ and $\rho(r) \approx \rho_l$, where ρ_g and ρ_l are the number densities of the bulk coexisting gas and liquid. Coexistence for the confined fluid occurs when $\Omega_g = \Omega_l$ or when $p - p^\dagger = 2(\sigma_{wg} - \sigma_{wl})/L$, the Laplace pressure difference across the cylindrical meniscus in the slit [15, 17, 18]. The use of Young's equation $\sigma_{wg} = \sigma_{wl} + \sigma_g \cos \theta$ and the relation $(\partial p / \partial \mu)_T = \rho$ then yields (1). Clearly (1) is valid provided $T \ll T_{c,L}$, the capillary critical temperature, so that any effects of shifted bulk criticality can be neglected. Does this approximation incorporate properly the effects of adsorption in the confined system? Formally we have, at fixed T ,

$$\frac{\Omega_g}{A} = -pL + \sigma_g(L, \mu) \quad (3)$$

where $\sigma_g(L, \mu)$ is the surface excess grand potential per unit area, along with the corresponding equation for Ω_l . The total adsorption $\Gamma = -(\partial \sigma / \partial \mu)_{L,T}$. Equations (2) make the simplest possible (zeroth order) approximations for $\sigma_g(L, \mu)$ and $\sigma_l(L, \mu)$. We now consider possible improvements.

Suppose first that $\theta > 0$ (partial wetting) so that in the limit $L \rightarrow \infty$ and $\mu \rightarrow \mu_{\text{sat}}^-$ the thickness of an adsorbed film l approaches a finite value $l_\infty(\mu_{\text{sat}})$. It is convenient to define the film thickness from the adsorption via

$$\Gamma_g = \int_0^L dz (\rho(z) - \rho_b) \equiv 2(\rho_l - \rho_g)l$$

where ρ_b is the bulk gas density for given (μ, T) and the fluid density profile $\rho(r) \equiv \rho(z)$ is assumed to vary only in the direction normal to the walls. Under these circumstances

we can make the following approximation

$$\begin{aligned}\sigma_g(L, \mu^*) &\approx \sigma_g(\infty, \mu^*) \\ &= \sigma_g(\infty, \mu_{\text{sat}}) + \left(\frac{\partial \sigma_g}{\partial \mu}\right)_{\text{sat}} (\mu^* - \mu_{\text{sat}}) + \dots \\ &= 2\sigma_{\text{wg}} - 2l_{\infty}(\mu_{\text{sat}})(\rho_l - \rho_g)(\mu^* - \mu_{\text{sat}}) + \dots\end{aligned}\quad (4)$$

which ignores any effects of confinement (L dependence) in the excess grand potential but does incorporate μ dependence. For strongly adsorbing walls Γ_g and, hence $l_{\infty}(\mu_{\text{sat}})$, can be large but necessarily remain finite. This would be the case for a fluid that undergoes a continuous (critical) wetting transition at some temperature T_w [22]. For $T \approx T_w$, $l_{\infty}(\mu_{\text{sat}})$ will then be substantial. By contrast we expect the adsorption on the 'liquid' branch Γ_l to be rather small so that we neglect the corresponding correction term and set $\sigma_l(L, \mu^*) \approx 2\sigma_{\text{wl}}$, as in (2b). With these assumptions coexistence now occurs for

$$\mu^* - \mu_{\text{sat}} = -2\sigma_{\text{lg}} \cos \theta / (L - 2l_{\infty}(\mu_{\text{sat}}))(\rho_l - \rho_g) \quad L \rightarrow \infty. \quad (5)$$

The term $L - 2l_{\infty}(\mu_{\text{sat}})$ which replaces L in the denominator of the Kelvin equation has an appealing geometrical interpretation: $A(L - 2l_{\infty})$ is the effective volume for 'gas' in the presence of thick adsorbed films. Note that (5) should remain valid, with the same coefficient of l_{∞} , for any form of fluid-fluid and wall-fluid forces and all dimensionalities d , provided the walls are partially wet. Any corrections to (5) that arise from including explicit finite-size effects in $\sigma_g(L, \mu)$ should be of higher order in (l_{∞}/L) . It follows that if we define an amplitude ϕ via the general expansion

$$\mu^* - \mu_{\text{sat}} = \frac{-2\sigma_{\text{lg}} \cos \theta}{(\rho_l - \rho_g)L} \left(1 - \frac{\phi l(\mu^*)}{L} + \dots\right) \quad (6)$$

then ϕ takes the trivial geometric value $\phi^{\text{geom}} = 2$ for any partial wetting situation $\theta > 0$. In this case the film thickness at coexistence in the confined system $l(\mu^*) \approx l_{\infty}(\mu_{\text{sat}})$ (is finite) in the limit $L \rightarrow \infty$.

The situation of complete wetting $\theta = 0$ is much more subtle and interesting. As is implied by (6) we expect such an expansion to remain valid but now $l_{\infty}(\mu_{\text{sat}}) = \infty$ so that the argument leading to (5) and the result $\phi = 2$ is no longer applicable. Recall that for complete wetting and $L = \infty$ the wetting film thickens as $l_{\infty}(\mu) \sim (\mu_{\text{sat}} - \mu)^{-\beta_s^{\text{co}}}$. The critical exponent β_s^{co} depends on the form of the fluid-fluid and wall-fluid forces as well as the dimensionality d [22, 23]. In $d = 3$ β_s^{co} is non-universal; $\beta_s^{\text{co}} = 0(\ln)$ for short-ranged forces whilst $\beta_s^{\text{co}} = 1/m$ for wall-fluid and fluid-fluid potentials that decay as $-z^{-m}$ ($m = 3$ for non-retarded dispersion forces). These are mean-field exponents but incorporating fluctuations does not alter them. The upper critical dimension for complete wetting with long-ranged forces is $d_s^{\text{co}} = 3 - 4/(m + 1)$ [23, 24]. For short-ranged forces $d_s^{\text{co}} = 3$ but the fluctuations alter only the amplitude of l_{∞} [22, 23]. This suggests that mean-field treatments of corrections to the Kelvin equation for capillary condensation should remain valid in $d = 3$. Let us recall then the classic Derjaguin derivation [16, 17, 25†].

† [25] extends Derjaguin's earlier work [16] and discusses the form of the disjoining pressure when dispersion and other forces operate.

For thick wetting films of thickness l at each wall the excess grand potential is conveniently expressed as

$$\sigma_g(L, \mu) \equiv 2\sigma_{wg} - 2p^\dagger l + 2pl + g(L, l) \quad (7)$$

where $g(L, \mu)$ is an excess free energy per unit area, defined via (7), and $l = l(\mu)$. The equilibrium film thickness l_0 is given by minimizing Ω_g with respect to l at fixed (μ, T) , i.e.

$$p - p^\dagger = -\frac{1}{2} \frac{\partial}{\partial l} g(L, l)|_{l_0} \equiv \Pi(L, l_0) \quad (8)$$

where $\Pi(L, l)$ is the disjoining pressure [25]. Similarly the Gibbs adsorption equation implies that at equilibrium $\Gamma_g \approx 2(\rho_l - \rho_g)l_0$. What is required is a suitable approximation for $g(L, l)$ or, equivalently, for the disjoining pressure. The simplest approximation [25] sets $g(L, l) = 2g(\infty, l)$, which implies finite-size effects can be neglected again. For dispersion forces in $d = 3$ it is well known that $g(\infty, l) = Al^{-2}/2$ where A is a positive constant. Substituting this form into (8) yields

$$p - p^\dagger \approx (\mu_{\text{sat}} - \mu)(\rho_l - \rho_l) = Al_0^{-3} \quad (9)$$

which is the standard growth law ($\beta_s^{\text{co}} = \frac{1}{3}$) for a complete wetting film at a single wall. Using this approximation for the confined 'gas' and setting $\sigma_l(L, \mu) \approx 2\sigma_{wl}$, as previously, we find coexistence when

$$p - p^\dagger = (2(\sigma_{wg} - \sigma_{wl}) + 2g(\infty, l(\mu^*))) / (L - 2l(\mu^*)) \quad (10)$$

or when

$$p - p^\dagger = 2\sigma_{lg} / (L - 3l(\mu^*)). \quad (11)$$

Thus, for dispersion forces the amplitude in (6) is $\phi = 3$. More generally, if the wall-fluid and fluid-fluid potential vary as $-z^{-m}$, so that $g(\infty, l) = Al^{-(m-1)}$, we find the denominator in (11) becomes $L - (2 + 2(m-1)^{-1})l(\mu^*)$ and

$$\phi^{\text{MF}} = 2 + 2/(m-1) \quad \text{long-ranged forces.} \quad (12)$$

The equivalent approximation for short-ranged forces is $g(L, l) \approx 2g(\infty, l) = A \exp(-\lambda l)$ which yields [16, 17]

$$p - p^\dagger = 2\sigma_{lg} / (L - 2l(\mu^*) - 2\lambda^{-1}). \quad (13)$$

Since λ^{-1} is a constant (microscopic) length (13) implies

$$\phi^{\text{MF}} = 2 \quad \text{short-ranged forces.} \quad (14)$$

Another result which emerges from the mean-field treatment is that wetting films are slightly thicker, for a given undersaturation, in slits than at a single wall, i.e. $l(\mu) > l_\infty(\mu)$. This observation follows from including terms of the form $-A(L-l)^{-(m-1)}$ in $g(L, l)$ [17, 18, 25]. It does not affect the validity of (12) and (14), however. We conclude that in a complete wetting situation the simple geometrical result for the amplitude, $\phi = 2$, is only obeyed for short-ranged forces when $d \geq 3$.

We return now to $d = 2$ where interfacial fluctuations in the wetting films are much stronger and we might expect significant fluctuation corrections to emerge. Now $d(=2) < d_c^{\text{co}}$ for both short-ranged forces and dispersion forces; recall $m = 4$ for the latter in two dimensions, implying $d_c^{\text{co}} = \frac{1}{5}$. The complete wetting exponent takes the universal value $\beta_s^{\text{co}} = \frac{1}{3}$ provided $m > 3$ so that fluctuations dominate [23, 24]. It is

possible to understand these results from a phenomenological viewpoint [26] by considering an excess free-energy (for a single wall)

$$g(\infty, l) = Al^{-(m-1)} + Bl^{-\tau} \quad (15)$$

where an effective repulsive interaction, that accounts for the entropy of the unbinding interface, has been added to the leading long-ranged potential energy term. The interaction exponent for thermal wandering is $\tau = 2(d-1)/(3-d)$, which is 2 for $d = 2$. If this second (entropic) term dominates one finds, from minimization of $\sigma_g(\infty, \mu)$, that $l_0 \sim (\mu_{\text{sat}} - \mu)^{-1/(\tau+1)}$, i.e. $\beta_s^{\text{co}} = \frac{1}{3}$ in $d = 2$. This procedure serves to *define* the weak fluctuation regime (WFR) for complete wetting [26]; the critical behaviour is obtained in mean-field fashion but with the entropic term replacing the direct interaction and *determining the exponents when $\tau < m - 1$.*

For the confined fluid the corresponding expansion is

$$g(L, l) = A[l^{-(m-1)} - (L-l)^{-(m-1)}] + B[l^{-\tau} - (L-l)^{-\tau}] + \dots \quad (16)$$

and it is assumed that there are no 'interference' effects associated with the entropy of the two unbinding interfaces. The derivation proceeds as previously and one finds, for $\tau < m - 1$ where fluctuations dominate, capillary coexistence with an amplitude

$$\phi = 2 + 2/\tau \quad \text{WFR} \quad (17)$$

i.e. ϕ takes the universal value 3 in $d = 2$. Note that this argument assumes any fluctuation contributions in the 'liquid' phase are irrelevant since thick 'drying' films do not develop.

3. Explicit results in $d = 2$

Ideally we would like to compare the prediction (6) (with $\phi = 3$) with exact results for, say, an infinitely long Ising strip with identical contact fields h_1 acting at both edges. Such results do not exist. Monte Carlo simulations for $M \times L$ lattices, with $M \gg L$ and periodic boundary conditions along the strip, have been performed [27]. Very sharp transitions (the rounding was not ascertained) were observed at bulk magnetic fields H^* that are shifted from the value $H = 0$ of the bulk first-order transition. The zeroth-order (Kelvin) prediction $H^* \sim L^{-1}$ is reasonably well verified and an attempt was made to ascertain the leading-order correction in the completely wet regime. Albano *et al* [27] used scaling arguments to suggest this correction should be proportional to $L^{-5/3}$ and their simulation data do give some support to this result. Our present treatment differs from that in [27] (those authors do not discuss the amplitude ϕ) but it does predict the same $L^{-5/3}$ correction. This follows from (6) noting that $l(\mu^*) \sim (\mu_{\text{sat}} - \mu^*)^{-1/3} \sim L^{1/3}$ in $d = 2$. In the absence of explicit results for the Ising strip we turn to a simpler, interfacial Hamiltonian which does admit an exact solution for pseudo-phase coexistence in $d = 2$.

It is convenient to consider first a model where the confined 'gas' phase exhibits a single liquid-gas interface. We suppose the surface fields h_1 and h_2 are such that wall 1 at $z = 0$ is completely wet by liquid ($\theta_1 = 0$ for $L = \infty$ and $\mu = \mu_{\text{sat}}^-$) while the second is partially wet. Furthermore we suppose that the second wall, at $z = L$, is not completely dry, i.e. the appropriate contact angle satisfies $\pi > \theta_2 > 0$. The temperature T must lie below any (critical) drying temperature T_D of the second wall. Such a 'gas' phase will exhibit a thick liquid film with interface near the first wall and should exhibit

pseudo-coexistence with a 'liquid' whose density profile is almost constant except near the second wall where a thin gas film can develop. The important microscopic configurations of such a system should be those associated with the confinement of the fluctuating interface. Consequently we would hope to capture the essential physics by employing a continuum capillary-wave-Hamiltonian, e.g. [22-24]

$$H_{CW}\{l(x)\} = \int_{-\infty}^{\infty} dx \left[\frac{\sigma_{lg}}{2} \left(\frac{dl}{dx} \right)^2 + U_B(l) \right] \quad (18)$$

where $l(x)$ denotes the distance of the liquid-gas interface from the wall at $l=0$ and x is measured along the wall. The binding potential is chosen to be $U_B(L; l) = Hl + U_w(L; l)$, with bulk field $H = (\mu_{\text{sat}} - \mu)(\rho_l - \rho_g)$ and

$$U_w(L; l) = \begin{cases} \infty & l < 0 \\ 0 & 0 < l < L - R \\ -\varepsilon & L - R < l < L \\ \infty & l > L \end{cases} \quad (19)$$

The well depth ε and width R must be chosen so that $\varepsilon > \pi^2(k_B T)^2/8R^2\sigma_{lg}$ [28] to ensure $T < T_D$. Pseudo-phase coexistence does occur in this model for certain values of (H, L) and the coexisting phases do have the form described above.

We would expect the Hamiltonian (18) to account for corrections to the Kelvin equation arising from interfacial fluctuations occurring in the 'gas' phase; again we suppose there are no fluctuations in the 'liquid' phase. Moreover, the potential (19) should suffice to describe long-ranged wall-fluid and fluid-fluid forces throughout the WFR since the complete wetting transition is determined by the entropic repulsion $l^{-\tau}$ rather than 'direct' interactions between the unbinding surfaces; long-ranged operators of the form $l^{-(m-1)}$ ($m > 3$) that might augment (19) would be irrelevant in a renormalization group sense [26]. Obtaining the solution of the Hamiltonian (18) is straightforward using transfer matrix techniques of the type described in [24]. One finds that for $T < T_D$, pseudo-phase coexistence, characterized by an exponentially large correlation length

$$\frac{\xi_{\parallel}}{R} \sim \left(\frac{L}{R} \right)^{1/3} \exp(cL/R) \quad (20)$$

occurs in the limit $L \rightarrow \infty$ for bulk fields that are exponentially close, $O(R/\xi_{\parallel})$, to

$$H^* = \frac{\tilde{A}}{L - \frac{3}{2}l_{\infty}(\mu^*)} \quad (21)$$

where the amplitudes $c \sim (T_D - T)$ and \tilde{A} are non-universal. The coefficient $\frac{3}{2}$ in the denominator is universal (throughout the WFR) and is different from the geometrical value of unity—we have a *single* complete wetting film in this case. The simplest extension of the Kelvin equation to this asymmetrically confined fluid would replace $2\sigma_{lg} \cos \theta$ in (1) by $\sigma_{lg}(\cos \theta_1 + \cos \theta_2)$. But we have chosen the binding potential in (18) so that $\theta_1 = 0$ and $\theta_2 < \pi$. As $T \rightarrow T_D^-$, so that $\theta_2 \rightarrow \pi$, $\cos \theta_2 + 1 \sim (T_D - T)^{2-\alpha_s}$, where the exponent $\alpha_s = 0$ for critical wetting (or drying) in $d = 2$ [22, 23]. The calculated amplitude $\tilde{A} \sim (T_D - T)^2$ does vanish with the exponent that is suggested by this argument. It is important to recognize that any value of H^* that does not satisfy (21), i.e. that does not incorporate the proper correction term, does not yield an exponentially large correlation length; the rounding of the transition is exponentially small as expected.

We return now to the original case of identical walls where both contact angles $\theta = 0$. Fluctuations now occur in wetting films on both sides of the slit. Given that these films have a thickness $l(\mu^*) \sim L^{1/3}$ at pseudo-phase coexistence we expect no significant entropic interference effects between the two films in the 'gas' phase and it should be valid to replace $l_\infty(\mu^*)$ by $l(\mu^*)$ in the limit of large L . It follows that although we do not have an explicit solution for a model with identical walls, we expect to recover the modified Kelvin equation (6) with $\phi = 3$ in $d = 2$. The result from the capillary-wave Hamiltonian lends strong support to our earlier prediction. We emphasize once again that the corrections to the zeroth-order Kelvin equation, as described by the amplitude ϕ , must be retained in order to obtain an exponentially large ξ_{\parallel} . These corrections contain crucial information about fluctuations which must be included for a self-consistent determination of $\mu^*(L, T)$.

4. Corrections for interfacial wandering in random media

So far we have considered pure fluids where the interfacial fluctuations are those associated solely with *thermal* wandering. There is a substantial literature concerning interfaces in impure systems or, more precisely, in quenched random media [29] where an interfacial Hamiltonian such as (18), or its generalization to higher dimension, now includes a random potential $U_R(l, x)$ acting on the interface and where the fluctuations of U_R are usually correlated to correspond to random fields or random bonds. Complete (and critical) wetting at a single wall has been discussed [29, 30] for both types of randomness in terms of the excess free energy (15). The contribution from interfacial wandering is still written as $Bl^{-\tau}$ but the interaction exponent τ no longer takes the value for thermal wandering, rather it is given by [29, 30]

$$\tau = 2(1 - \zeta)/\zeta \quad (22)$$

where ζ is the interface wandering or roughness exponent defined generally via the relation $\xi_{\perp} \sim \xi_{\parallel}^{\zeta}$, which expresses the extent of the perpendicular excursions of the interface (roughness) ξ_{\perp} , in terms of a characteristic transverse (correlation) length ξ_{\parallel} . For thermal wandering standard capillary-wave analysis yields the familiar result $\zeta_{\text{th}}(d) = (3 - d)/2$ for $1 \leq d \leq 3$, whereas for random-fields heuristic arguments [29] yield $\zeta_{\text{RF}}(d) = (5 - d)/3$ for $2 \leq d \leq 5$. For random bonds Fisher [29] quotes $\zeta_{\text{RB}}(2) = \frac{2}{3}$ and $\zeta_{\text{RB}}(3) \approx 0.4$, with $\zeta_{\text{RB}}(d) = 0$ for $d \geq 5$. By comparing the corresponding values of τ , obtained from (22), with the long-ranged force exponent $m - 1$ entering (15), one can determine whether or not long-ranged forces are relevant for complete wetting in random media [29, 30].

We can extend this strategy to capillary condensation by adopting the same procedure we employed for thermal wandering, i.e. we employ (16) and neglect 'interference' effects. Clearly for $\tau < m - 1$ we recover the modified Kelvin equation (6) with the amplitude ϕ given by

$$\phi = 2 + 2/\tau = \frac{2 - \zeta}{1 - \zeta} \quad \text{fluctuation dominated.} \quad (23)$$

In table 1 we summarize our results for this ratio in the case of short-ranged forces. Random fields give rise to the largest correction to the geometrical result $\phi^{\text{geom}} = 2$ since $\tau_{\text{RF}}(d) < \tau_{\text{RB}}(d) < \tau_{\text{th}}(d)$ for $2 \leq d < 5$. In $d = 2$ random fields destroy the interface and, hence, the gas-liquid transition. Incorporating long-ranged dispersion forces will

Table 1. The amplitude ϕ that determines corrections to the Kelvin equation: short-ranged forces.

Bulk dimension	$d = 2$	$d = 3$	$d = 4$	$d = 5$
Pure system	3†	2	2	2
Random fields	—	4	$\frac{5}{2}$	2
Random bonds	4	$\sim 2.7\ddagger$	$\sim 2.2\ddagger$	2

† In $d = 2$ pseudo-phase coexistence occurs for the confined pure fluid whereas for higher dimensions true coexistence should occur.

‡ These values are based on estimates of ζ given in [29].

not affect the values of ϕ in $d = 2$. However, in $d = 3$ dispersion forces will give rise to non-universal mean-field values of ϕ for pure systems and random bonds; only for random fields will the value $\phi = 4$ remain insensitive to the presence or absence of long-ranged forces.

5. Concluding remarks

In this paper we have argued that interfacial fluctuations in complete wetting films lead to corrections to the macroscopic Kelvin equation for capillary condensation in slits that are of a similar type to those derived originally by Derjaguin [16] in his mean-field treatment of long-ranged wall–fluid and fluid–fluid forces. The effective slit width for ‘gas’ is $L - \phi l(\mu^*)$ where the amplitude ϕ is given by

$$\phi = \begin{cases} (d+1)/(d-1) & 1 < d \leq 3 \\ 2 & d \geq 3 \end{cases} \quad (24)$$

for pure systems with short-ranged forces. In $d = 2$ thermal wandering is predicted to give rise to the result $\phi = 3$ throughout the wFR, i.e. even in the presence of dispersion forces, and this is supported by explicit analysis of a capillary-wave Hamiltonian. That analysis also points out the necessity of retaining the corrected width $L - 3l(\mu^*)$ if one is to obtain the exponentially large transverse correlation length which defines the pseudo-phase coexistence in $d = 2$. Interfacial wandering in random media should lead to more pronounced corrections; ϕ is calculated to be larger. In particular, random fields in $d = 3$ should yield the universal value $\phi = 4$.

Some of our predictions should, in principle, be amenable to test via Monte Carlo simulation for Ising lattices. Previous work [19] for a three-dimensional system with a $-z^{-3}$ wall-particle potential showed that the Derjaguin correction, $\phi = 3$, did yield a value of μ^* closer to simulation than did the geometric correction $\phi^{geom} = 2$, but the wetting films were still rather thin. In order to ascertain corrections due to interfacial fluctuations large lattices in $d = 2$ would appear to offer the best possibility. Extension or re-analysis of the simulations of Albano *et al* [27] might be profitable. Complications of finite transverse length M plus the need to have L sufficiently large to observe thick films might prove prohibitive, however.

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