

Comment on “Simple theory for the critical adsorption of a fluid”

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(Received 12 November 1985)

Henderson [Phys. Rev. A 32, 2336 (1985)] has proposed that the critical exponent for adsorption should be either  $\gamma$  or  $\gamma/2$ , where  $\gamma$  is the (bulk) compressibility exponent. It is shown that both results are artifacts of the mean spherical approximation (MSA) employed by Henderson. The MSA, and closely related closures of the wall-particle Ornstein-Zernike equation, are essentially linear-response approximations which neglect nonlinearities that are crucial in critical adsorption, even at the mean-field level. Our argument is made explicit by re-deriving the correct (Fisher—de Gennes) exponent  $\nu-\beta$  and illustrating the failings of linearized treatments. Since the latter also fail to describe complete wetting, their validity is restricted to states well removed from bulk two-phase coexistence.

In a recent paper Henderson<sup>1</sup> has argued that the adsorption  $\Gamma$  of a near-critical fluid at a wall should diverge as  $|T - T_c|^{-x}$  with an exponent  $x$  that is either  $\gamma$  or  $\gamma/2$ , where  $\gamma(\simeq 1.24)$  is the (bulk) compressibility exponent. Both results differ from the well-known Fisher—de Gennes<sup>2</sup> result  $x = \nu - \beta$ , where  $\nu(\simeq 0.63)$  and  $\beta(\simeq 0.32)$  are the (bulk) correlation-length and order-parameter exponents, respectively. Henderson’s argument is based on a mean spherical approximation (MSA) closure of the exact wall-particle Ornstein-Zernike equation in which the adsorbing wall is regarded as the limit of a giant host particle dissolved in the fluid.<sup>3,4</sup> While such approximate closures are known to yield results in good agreement with computer simulations for *certain* adsorption problems,<sup>5,6</sup> they fail totally<sup>7</sup> in problems which involve complete wetting of the wall-fluid interface. Such problems include the growth of a (macroscopic) thick film of liquid at a wall-gas interface and of a thick film of gas at a wall-liquid interface, as coexistence is approached. The approximation schemes fail because they are essentially linear-response theories;<sup>8</sup> they cannot account for the development of the second (interfacial) phase that is associated with a second minimum in the grand-potential density<sup>9</sup>  $\omega$  and therefore describe only fluid states that can be reached by means of linear response about the bulk fluid, i.e., the first minimum of  $\omega$ . Given this failing it seems very unlikely that such an approximation scheme could describe properly the decay of the density profile and the resulting divergence of  $\Gamma$  that occurs when the two minima coalesce and the two phases merge into a single fluid phase at the critical point. Here we show that this is indeed the case and that Henderson’s approach predicts erroneous critical exponents which result from the neglect of crucial nonlinearities that are a fundamental feature of adsorption in the critical region, even at the level of mean-field approximation.

Henderson’s results can be written as

$$\Gamma_{l,r} = \frac{C_1}{a} + \frac{C_2}{a^2} \tag{1a}$$

and

$$\Gamma_{s,r} = \frac{C}{a}, \tag{1b}$$

where

$$a^2 = \frac{1}{k_B T} \left[ \frac{\partial p}{\partial \rho_b} \right]_T = \frac{1}{k_B T} \rho_b \left[ \frac{\partial \mu}{\partial \rho_b} \right]_T,$$

is proportional to the inverse compressibility of the bulk fluid, and  $C, C_1,$  and  $C_2$  are quantities which remain finite at coexistence ( $T < T_c$ ) and at the critical temperature  $T = T_c$ . Equation (1a) is supposed to be appropriate for wall-fluid potentials with a long decay length whereas (1b) is appropriate when this potential is shorter ranged. Since  $a^2$  vanishes as  $|T - T_c|^\gamma$ , Eqs. (1a) and (1b) predict  $x = \gamma$  and  $\gamma/2$ , respectively. Before discussing the shortcomings of these results it is instructive to examine the subcritical adsorption in the limit  $p \rightarrow p_{\text{sat}}$ , the saturated vapor pressure (or  $\mu \rightarrow \mu_{\text{sat}}$ ). For sufficiently high temperatures, but still below  $T_c$ , the wall-gas interface will be wet completely by a film of liquid and  $\Gamma$  will diverge as

$$- |T - T_c|^{-\nu+\beta} \ln(|\mu_{\text{sat}} - \mu|)$$

provided the wall-fluid potential decays exponentially,<sup>10</sup> as assumed by Henderson. No such divergence is predicted by (1a) or (1b). These can only give a divergent adsorption at a bulk spinodal,<sup>11</sup> i.e., inside the coexistence curve. Thus, as stated earlier, the approximations fail to account for complete wetting; they do not incorporate information about the second phase.<sup>7</sup>

Turning now to the critical region, it is easy to understand the origin of the  $|T - T_c|^{-\gamma}$  divergence given by the second term in (1a). In the wall-particle description

$$\Gamma = \rho_b \int_0^\infty dz h_{\text{wf}}(z),$$

where  $h_{wf}$  is the total correlation function for the wall-fluid correlations and the integration is over the region outside the wall ( $z > 0$ ).  $\rho_b$  is the bulk fluid density. At the critical point the fluid-fluid correlation function  $h_{ff}$  is long ranged so that

$$\rho_b \int d\mathbf{r} h_{ff} \sim a^{-2} \sim |T - T_c|^{-\gamma}.$$

The linear character of the closure approximations ensures that  $h_{wf}$  exhibits equivalent long-ranged decay, so that  $\Gamma$  diverges in the same fashion as the compressibility. In reality the divergence of  $\Gamma$  is much weaker because of nonlinear effects. We made this argument explicit by reference to a simple (square-gradient) density-functional theory of the wall-fluid interface.<sup>10,12</sup> Although such theories cannot describe the oscillations in the density profile near the wall, which arise from short-ranged correlations, this deficiency is not important for wetting or for critical adsorption both of which are dominated by a slow decay of the profile at large distances from the wall. The grand potential functional is

$$\frac{\Omega[\rho]}{\mathcal{A}} = \int_0^\infty dz \left[ \frac{D}{2} \left( \frac{d\rho}{dz} \right)^2 + \omega(\rho(z)) \right] + \Phi(\rho_w), \quad (2)$$

where  $\mathcal{A}$  is the total wall surface area and  $\omega(\rho)$  is the grand-potential density.<sup>9</sup>

It is assumed that wall-fluid forces are sufficiently short ranged that these can be incorporated into a function  $\Phi$  that depends only on  $\rho_w = \rho(0)$ , the density at the wall. The equilibrium profile, given by minimization of (2), satisfies

$$D \frac{d^2 \rho}{dz^2} = \frac{d\omega(\rho)}{d\rho} \quad (3a)$$

with the boundary condition at  $x = 0$ ,

$$D \left[ \frac{d\rho}{dz} \right]_{z=0} = \frac{d\Phi}{d\rho_w}. \quad (3b)$$

Equation (3a) has a first integral

$$\frac{D}{2} \left[ \frac{d\rho}{dz} \right]^2 = \omega(\rho) - \omega(\rho_b) \equiv \psi(\rho) \quad (4)$$

which satisfies the boundary condition in the bulk fluid;  $-\omega(\rho_b) = p$ , the bulk pressure for given  $\mu$  and  $T$ . Given  $\omega(\rho)$ , Eq. (4) is readily integrated<sup>12</sup> to yield  $z(\rho)$ . The adsorption

$$\Gamma = \int_0^\infty dz [\rho(z) - \rho_b]$$

can be expressed as

$$\Gamma = \int_{\rho_b}^{\rho_w} d\rho (\rho - \rho_b) \left[ \frac{2\psi(\rho)}{D} \right]^{-1/2}. \quad (5)$$

For  $T < T_c$  and  $\mu \simeq \mu_{\text{sat}}$   $\psi(\rho)$  has two distinct minima. The first has  $\psi(\rho_b) = 0$ , corresponding to the bulk fluid phase, while the second,  $\psi(\rho^\dagger)$ , corresponds to the other phase. In the limit  $|\mu - \mu_{\text{sat}}| \rightarrow 0$ ,  $\psi(\rho^\dagger) \rightarrow 0$  and complete wetting occurs if the integration path in (5) passes through this second minimum.<sup>12</sup> As  $T \rightarrow T_c$  the minima coalesce and it is instructive to make a standard, nonclassical, expansion about the critical density  $\rho_c$ ,

$$\omega(\rho) = \omega(\rho_c) + \frac{a'}{2} (\rho - \rho_c)^2 + \frac{b}{\delta + 1} (\rho - \rho_c)^{\delta + 1} - h(\rho - \rho_c), \quad (6)$$

where  $a' \equiv (\partial\mu/\partial\rho)_T$  at  $\rho = \rho_c$  and  $h = \mu - \mu_{\text{co}}$ , with  $\mu_{\text{co}}$  the chemical potential at coexistence.  $\delta (\simeq 4.8)$  is the usual critical exponent. In mean-field approximation  $\delta = 3$  and  $b = \frac{1}{6} (\partial^3\mu/\partial\rho^3)_T$  at  $\rho = \rho_c$ . The adsorption then becomes

$$\Gamma = \left[ \frac{D}{2} \right]^{1/2} \int_{\tilde{\rho}_b}^{\tilde{\rho}_w} d\tilde{\rho} (\tilde{\rho} - \tilde{\rho}_b) \left[ \frac{a'}{2} (\tilde{\rho}^2 - \tilde{\rho}_b^2) + \frac{b}{\delta + 1} (\tilde{\rho}^{\delta + 1} - \tilde{\rho}_b^{\delta + 1}) - h(\tilde{\rho} - \tilde{\rho}_b) \right]^{-1/2} \quad (7)$$

with  $\tilde{\rho} = \rho - \rho_c$ . The nature of the critical divergence can be ascertained by taking  $h = 0$  and  $T \rightarrow T_c^+$ . Then  $a'$  vanishes as  $|T - T_c|^\gamma$  and

$$\Gamma \sim \left[ \frac{D}{2} \right]^{1/2} \left[ \frac{b}{\delta + 1} \right]^{-1/2} \tilde{\rho}_b^{-2 - (\delta + 1)/2} \times \int_1^{y_w} dy \frac{(y - 1)}{(y^{\delta + 1} - 1)^{1/2}}.$$

But  $\tilde{\rho}_b \sim |T - T_c|^\beta$  and  $D \sim |T - T_c|^{-\nu\eta}$ , where  $\eta (\simeq 0.03)$  is the exponent<sup>13</sup> describing the decay of  $h_{ff}(r)$  at  $T = T_c$ , so that  $\Gamma \sim |T - T_c|^{-x}$ , with

$$x = [\nu\eta + \beta(\delta - 3)]/2.$$

Using the scaling relations  $\gamma = (\delta - 1)\beta$  and  $-\nu\eta = \gamma - 2\nu$  it follows that  $x = \nu - \beta$ , the result obtained by Fisher and de Gennes<sup>2</sup> from a different scaling argument. In mean-field approximation  $\eta = 0$ ,  $\delta = 3$ , and  $x = 0$ , implying a logarithmic divergence of  $\Gamma$ . This is confirmed by direct integration of (5), employing (6) with  $\delta = 3$ ,  $h = 0$ , and  $\rho_b = \rho_c$ . We find  $\Gamma \sim -\ln a'$ , with  $a' \sim |T - T_c|$  in mean-field approximation. It is well known<sup>2</sup> that these characteristic divergences of the adsorption are a consequence of a particular slow decay of the profile to its bulk value,

$$\rho(z) - \rho_b \sim \begin{cases} (\sigma/z)^{\beta/\nu} & \text{for } \sigma \ll z \ll \xi \text{ or } T = T_c \\ e^{-z/\xi} & \text{for } z \gg \xi, \end{cases}$$

where  $\xi$  is the bulk correlation length and  $\sigma$  is a molecular size. Such decay stems from the term in  $(\rho - \rho_c)^{\delta+1}$  in (6). Its origin is rather more transparent in the mean-field analysis<sup>14</sup> of (4) where the quartic term produces a decay  $\rho(z) - \rho_b \sim \sigma/z$ .

It is evident that a satisfactory treatment of both wetting and critical adsorption must incorporate a realistic grand-potential density. However, the MSA and related closure approximations of the wall-particle Ornstein-Zernike equation yield  $\omega(\rho)$  with only a single minimum at  $\rho = \rho_b$  for all temperatures.<sup>7,8</sup> The Percus-Yevick MSA result<sup>7</sup> is the parabola

$$\omega_{PY}(\rho) = \omega(\rho_b) + \frac{1}{2}(\rho - \rho_b)^2 \left[ \frac{\partial \mu}{\partial \rho_b} \right]_T,$$

which is completely unrealistic. If this were employed in (5) it would imply  $\Gamma \sim 1/a$ , i.e., a result similar to Eq. (1b). However, the wall-particle approach is not strictly equivalent to the square-gradient approximation so one must expect some modifications. In order to illustrate the deficiencies of an approach which does not include the quartic (or  $\rho^\delta$ ) terms in  $\omega(\rho)$  we substitute (6) in the equation of motion (3a)

$$D \frac{d^2 \tilde{\rho}}{dz^2} = a' \tilde{\rho} + b \tilde{\rho}^\delta - h \quad (8)$$

and linearize about the bulk, setting  $\tilde{\rho}(z) = \tilde{\rho}_b + S(z)$ , so that

$$D \frac{d^2 S}{dz^2} = (a' + \delta b \tilde{\rho}_b^{\delta-1}) S. \quad (9)$$

The surface free energy  $\Phi$  is often modeled<sup>12</sup> by  $\Phi = K \rho_w^2 / 2 - h_1 \rho_w$ , where  $h_1$  represents an incremental "magnetic" field acting on the surface layer and  $K$  is a strength parameter. Equation (3b) then becomes

$$D \left[ \frac{dS}{dz} \right]_{z=0} = K[\tilde{\rho}_b + S(0)] - h_1. \quad (10)$$

The required solution of (9) and (10) is

$$S(z) = \frac{(h_1 - K \tilde{\rho}_b)}{\lambda D + K} e^{-\lambda z},$$

with

$$\lambda^2 = (a' + \delta b \tilde{\rho}_b^{\delta-1}) / D,$$

and

$$\Gamma = \int_0^\infty dz S(z)$$

is simply

$$\Gamma = (h_1 - K \tilde{\rho}_b) / \lambda (\lambda D + K) \quad (11)$$

which can be made to yield two different critical exponents. If  $K = 0$ , then

$$\Gamma = h_1 / D \lambda^2 \sim |T - T_c|^{-\gamma},$$

whereas if  $K \neq 0$ ,  $\Gamma$  diverges as  $h_1 / K \lambda$  or

$$|T - T_c|^{-(\gamma + \nu\eta)/2}.$$

Setting  $\eta = 0$  we obtain both types of divergence suggested by Henderson.<sup>1</sup> Both arise as a result of the linearization of (8); both are artifacts.

We conclude that the MSA and related closure approximations are incapable of describing critical-point adsorption and complete wetting.<sup>15</sup> Their validity is restricted to states that are removed from bulk coexistence and from the critical point. For supercritical fluids such approximations might be qualitatively correct. Henderson<sup>1</sup> suggests that his result  $x = \gamma/2$  is in reasonable agreement with recent adsorption measurements by Blümel and Findenegg.<sup>16</sup> These authors find  $x \approx 0.5$  which is somewhat greater than  $\nu - \beta \approx 0.3$ , but suggest possible explanations of the discrepancy. We have shown that there is no reason to suppose that either  $x = \gamma$  or  $x = \gamma/2$  is the correct critical exponent for adsorption at a single wall. A proper explanation of the results of Ref. 16 must await further work.

#### ACKNOWLEDGMENT

This research was supported by the Science and Engineering Research Council of the United Kingdom.

<sup>1</sup>D. Henderson, Phys. Rev. A 32, 2336 (1985).

<sup>2</sup>M. E. Fisher and P. G. de Gennes, C. R. Acad. Sci. Paris Ser. B 287, 207 (1978).

<sup>3</sup>(a) See, e.g., D. Henderson, E. Waisman, and J. L. Lebowitz, in *Colloidal and Interface Sciences*, edited by M. Kerker (Academic, New York, 1976), Vol. 3, p. 37. (b) D. Henderson, J. L. Lebowitz, L. Blum, and E. Waisman, Mol. Phys. 39, 47 (1980).

<sup>4</sup>D. Henderson and I. K. Snook, J. Phys. Chem. 87, 2956 (1983).

<sup>5</sup>See, e.g., D. Nicholson and N. G. Parsonage, *Computer Simulation and the Statistical Mechanics of Adsorption* (Academic, New York, 1982), Chap. 7; J. E. Lane, T. H. Spurling, B. C. Freasier, J. W. Perram, and W. R. Smith, Phys. Rev. A 20, 2147 (1979).

<sup>6</sup>I. K. Snook and D. Henderson, J. Chem. Phys. 68, 2134 (1978).

<sup>7</sup>R. Evans, P. Tarazona, and U. Marini Bettolo Marconi, Mol. Phys. 50, 993 (1983). Although this paper places emphasis on the failings of the HNC and PY closure approximations of the wall-particle Ornstein-Zernike equation, equivalent failings occur in the MSA closure. The latter is obtained by linearization of the two former approximations.

<sup>8</sup>This becomes apparent when these approximations are derived from density-functional theory—see M. J. Grimson and G. Rickayzen, Mol. Phys. 42, 767 (1981); S. L. Carnie, D. Y. C. Chan, D. J. Mitchell, and B. W. Ninham, J. Chem. Phys. 74, 1472 (1981). The direct correlation function of the inhomogeneous fluid is approximated by that of the uniform (bulk) fluid and this restricts the applicability of the approximations

to problems involving a single phase—see Ref. 7 and J. R. Henderson, *Mol. Phys.* **52**, 1467 (1984).

<sup>9</sup>This is defined (Ref. 7) by  $\omega(\rho) = f(\rho) - \mu\rho$ , where  $f(\rho)$  is the Helmholtz free-energy density of a uniform fluid of density  $\rho$  and  $\mu$  is the chemical potential of the bulk fluid (reservoir).

<sup>10</sup>A faster, inverse-power-law divergence occurs for potentials that decay algebraically with distance from the wall—see, e.g., P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985), and references therein. Such potentials can also lead to subtle effects in critical adsorption which we do not consider here.

<sup>11</sup>The numerical results shown in Fig. 1 of Ref. 4 do indicate a diverging  $\Gamma$  for  $T = 0.97T_c$ . We suspect this occurs at the spinodal density.

<sup>12</sup>J. W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977) introduced such a Landau theory to describe the wetting transition and the accompanying divergence of  $\Gamma$  that occurs below  $T_c$ . A comprehensive review is given by D. E. Sullivan and M. M. Telo da Gama, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1986), p. 45.

<sup>13</sup>See, e.g., J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Oxford University, Oxford, 1982), Chap. 9.

<sup>14</sup>B. Widom, *J. Chem. Phys.* **67**, 872 (1977). Widom investigat-

ed the composition profile at the interface between a noncritical fluid phase and a critical phase using a free-energy functional of the type described here—see also Ref. 13. Our wall replaces his noncritical phase.

<sup>15</sup>Although some of the defects of the closure approximations and, in particular, their failure to account for thick adsorbed layers seem to have been recognized earlier by Henderson [Ref. 3(b)] these were not stated clearly. Other approximations due to W. A. Steele, in *The Solid-Gas Interface*, edited by E. A. Flood (Dekker, New York, 1966), Vol. 1, Chap. 10; F. M. Kuni and A. I. Rusanov, *Russ. J. Phys. Chem.* **42**, 443 (1968); **42**, 621 (1968); and M. J. Stott, E. H. Voice, and W. H. Young, *Phys. Chem. Liq.* **12**, 135 (1982) suffer from the same defects. The theory of ionic adsorption proposed by D. Henderson, J. Barojas, and L. Blum, *J. Phys. Chem.* **87**, 4544 (1983) is equivalent to the MSA closure of Ref. 4. Consequently the critical-point divergence of  $\Gamma_i$  is incorrectly described. The results of Fig. 2 of this paper indicate a diverging  $\Gamma_i$  at  $T = 0.99T_c$ ; we suspect this is associated with the spinodal.

<sup>16</sup>S. Blümel and G. H. Findenegg, *Phys. Rev. Lett.* **54**, 447 (1985).