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LETTER TO THE EDITOR

The critical exponent of Tolman's length

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Abstract. The change of surface tension with curvature is governed by a microscopic length, δ, introduced by Tolman. It is shown that this length diverges weakly at the liquid–gas critical point of the penetrable-sphere model, with an exponent $(\mu-\beta-1)$, where μ is the exponent of the surface tension, and β of the orthobaric densities. This result is compared with those derived from Landau–Ginzburg–Wilson Hamiltonians.

The surface tension of a spherical liquid drop, σ, and the radius at which it acts, the radius of tension R_σ, are related by the equations (Rowlinson and Widom 1982)

$$p^{\mathrm{l}}-p^{\mathrm{g}}=2\sigma/R_\sigma \qquad \text{(Laplace)} \tag{1}$$

$$\sigma=\sigma_\infty(1-2\delta/R_\sigma) \qquad \text{(Tolman)} \tag{2}$$

where p^{l} and p^{g} are the pressures in the homogeneous liquid within the drop and in the gas outside it, where σ_∞ is the tension of the planar surface ($R_\sigma=\infty$) at the same temperature, and where Tolman's length, δ, is given by

$$\delta=R_{\mathrm{e}}-R_\sigma=z_{\mathrm{e}}-z_\sigma. \tag{3}$$

Here R_{e} is Gibbs's equimolar surface:

$$\int_0^\infty R^2\,\mathrm{d}R(\rho(R)-\rho^{\mathrm{l,g}}(R))=0, \tag{4}$$

where $\rho(R)$ is the density at radius R, and

$$\begin{aligned}\rho^{\mathrm{l,g}}(R)&=\rho^{\mathrm{l}} \qquad (R<R_{\mathrm{e}}),\\ \rho^{\mathrm{l,g}}(R)&=\rho^{\mathrm{g}} \qquad (R>R_{\mathrm{e}}).\end{aligned} \tag{5}$$

Since equation (2) is valid only for first order in the curvature, $(1/R_\sigma)$, the length δ can be equated to the planar limit of $R_{\mathrm{e}}-R_\sigma$, namely $z_{\mathrm{e}}-z_\sigma$ for an interface in the x, y plane.

In a liquid at low temperatures, δ is the same order of magnitude, 10^{-10} m, as the range of the intermolecular forces, the statistical correlation length, ξ, and the thickness of the interface, D. Near the liquid–gas critical point the range of the forces is unchanged, but ξ and D diverge as $|t|^{-\nu}$, where $t=(T-T^{\mathrm{c}})/T^{\mathrm{c}}$ and $\nu\sim0.63$ in three dimensions. Fisher and Wortis (1984) have recently examined the critical behaviour of Tolman's length δ for a Landau–Ginzburg–Wilson (LGW) Hamiltonian with asymmetric operators, and deduced that

$$\delta\sim|t|^{\chi} \qquad \text{where} \qquad \chi=\theta_5-\nu \tag{6}$$

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and θ_5 (or Δ_5, or $-\phi_5$, or $-\lambda_5\nu$, in other notations) is the exponent associated with the leading asymmetric correction to scaling. In Landau, or mean-field approximation, $\theta_5 = \nu = \frac{1}{2}$, and δ tends to a finite non-zero length.

The purpose of this letter is to show that an exact expression for χ can be obtained for the penetrable-sphere model (Widom and Rowlinson 1970, Rowlinson 1980). This model comes in two forms, the primitive or two-component, and the transcribed, or one-component. The first is a binary mixture of particles with pair-additive potentials, $u_{\alpha\beta}(r)$, where r is the (continuous) separation:

$$\begin{aligned} &u_{aa}(r)=0, \qquad u_{bb}(r)=0, \\ &u_{ab}(r)=\infty \qquad (r<d), \qquad u_{ab}(r)=0 \qquad (r>d). \end{aligned} \tag{7}$$

The second is obtained by integrating over b-particles in the grand-partition function of the first to obtain that function for a one-component system with a more complicated multi-body potential which allows the particles to penetrate each other. The primitive version, for which an index (2) is used, has an obvious a–b symmetry which is hidden, but not lost, in the transcribed form, index (1).

At high activities, λ_a, λ_b, of both components, the primitive system forms two phases separated by a planar interface with a tension $\sigma^{(2)}(\lambda^{(2)})$, where $\lambda^{(2)}$ $(=\lambda_a=\lambda_b)$ is the common activity in both phases. By symmetry,

$$\rho_a(z-z_s)=\rho_b(z_s-z), \tag{8}$$

where z_s is the surface of symmetry, on which $\rho_a=\rho_b$. The surface of tension, z_σ, is a property of the whole system, and hence, by symmetry, coincides with z_s. The surface tension is given exactly (Hemingway *et al* 1983, equations (3.1)–(3.4)) by

$$\sigma^{(2)}(\lambda^{(2)})=2kT\int_{\lambda^{(2)c}}^{\lambda^{(2)}}(\rho_a^\alpha-\rho_a^\beta)\delta^{(2)}\,\mathrm{d}\ln\lambda, \tag{9}$$

where ρ_a^α is the density of component a in phase α, and

$$\delta^{(2)}=z_e^a-z_\sigma=z_e^a-z_s=-(z_e^b-z_\sigma)=-(z_e^b-z_s), \tag{10}$$

where z_e^a is the equimolar surface for component a. Let $l\equiv(\lambda^{(2)}-\lambda^{(2)c})/\lambda^{(2)c}$, and introduce the exponents

$$\sigma^{(2)}\sim|l|^{\mu^{(2)}}, \qquad (\rho_a^\alpha-\rho_a^\beta)\sim|l|^{\beta^{(2)}}, \qquad \delta^{(2)}\sim|l|^{\chi^{(2)}}. \tag{11}$$

Then equation (9) requires that

$$\chi^{(2)}=\mu^{(2)}-\beta^{(2)}-1. \tag{12}$$

These results can now be transcribed to those for the one-component version. The activity λ_b becomes a reciprocal temperature $\theta=\varepsilon/kT$, where ε is a characteristic energy, so that l becomes t. The activity λ_a becomes $\lambda\,\mathrm{e}^\theta$, where λ is the activity of the one-component version. The density ρ_a goes to ρ, and so $\beta^{(2)}=\beta^{(1)}$, and $z_e^a=z_e$. The surface tensions are the same, $\sigma^{(2)}=\sigma^{(1)}$, since there is a one-component equation that exactly parallels equation (9) (Leng *et al* 1976):

$$\sigma^{(1)}(\theta)=\frac{2}{\theta}\int_{\theta^c}^{\theta}(\rho^\mathrm{l}-\rho^\mathrm{g})(z_e-z_s)\,\mathrm{d}\ln\theta. \tag{13}$$

Note, however that equation (13) contains $(z_e - z_s)$, where z_s is the two-component plane of symmetry which is equal to $z_\sigma^{(2)}$, but which has still to be identified with $z_\sigma^{(1)}$. This identification can be made as follows.

The two-component interface, with $\lambda_a = \lambda_b$, can be bent isothermally to produce a drop of an a-rich phase in a b-rich medium by changing λ_a to λ_a^* at fixed λ_b, where $\lambda_a^* > \lambda_a$. The transcribed version is a drop of liquid in a gas with $\lambda^* = \lambda_a^* \, \mathrm{e}^{-\theta}$, and the same reciprocal temperature θ. If π denotes the pressure-to-temperature ratio then the transcription is

$$\begin{aligned} \pi^{(2)}[\lambda_a, \lambda_b] &= \pi^{(1)}[\lambda, \theta] + \theta, \\ \pi^{(2)}[\lambda_a^*, \lambda_b] &= \pi^{(1)}[\lambda^*, \theta] + \theta. \end{aligned} \tag{14}$$

It follows that the pressure drop across the curved surface is unchanged on transcription, and so from Laplace's equation (1),

$$\sigma^{(2)}/R_\sigma^{(2)} = \sigma^{(1)}/R_\sigma^{(1)}. \tag{15}$$

Tolman's equations in a d-dimensional system are

$$\frac{\sigma^{(2)}}{\sigma_\infty} = 1 - \frac{(d-1)(R_e - R_\sigma^{(2)})}{R_\sigma^{(2)}}, \qquad \frac{\sigma^{(1)}}{\sigma_\infty} = 1 - \frac{(d-1)(R_e - R_\sigma^{(1)})}{R_\sigma^{(1)}} \tag{16}$$

where R_e is the common equimolar radius (since $\rho_a = \rho$).

We now have three equations, (15) and (16), for the four unknowns $\sigma^{(1)}$, $\sigma^{(2)}$. $R_\sigma^{(1)}$ and $R_\sigma^{(2)}$. Put $R_\sigma^{(1)} = R_e(1+x_1)$ and $R^{(2)} = R_e(1+x_2)$, and re-arrange the equations to give

$$d(x_1 - x_2) = 2(x_1 - x_2)(1 + \tfrac{1}{2}x_1 + \tfrac{1}{2}x_2)(1 - x_1 x_2)^{-1}. \tag{17}$$

Clearly $x_1 = x_2$ unless $d = 2$, when the solution is undetermined to first order in the parameters x_1 and x_2; $x_1 \sim x_2 \ll 1$. If, however, $d \neq 2$, then it follows that $\sigma^{(1)} = \sigma^{(2)}$, $R_\sigma^{(1)} = R_\sigma^{(2)}$, and in the planar limit $z_\sigma^{(1)}$ is identified with z_s, since we know that $R_\sigma^{(2)}$ goes to $z_\sigma^{(2)} = z_s$. (There is no reason to believe that this is not true also for $d = 2$.) This completes the identification of physical properties, and so of their exponents. We have, dropping now the index (1),

$$\delta \sim |t|^\chi \qquad \text{where} \qquad \chi = \mu - \beta - 1. \tag{18}$$

In a mean-field approximation, $\mu = \frac{3}{2}$, $\beta = \frac{1}{2}$ and χ is again zero. Nicoll and Zia (1981) have obtained the ε-expansion of θ_5, and their result precludes the identification of $(\theta_5 - \nu)$ of equation (6) with $(\mu - \beta - 1)$ of equation (18). Since $\mu = 2 - \alpha - \nu$, the difference in the two expressions for χ is that of $(1-\alpha)$ from $(\theta_5 + \beta)$. This is just the difference found by Vause and Sak (1980) and Sak and Vause (1980) between the leading singular term in the orthobaric diameter, ρ_d, in the LGW model, and that for the penetrable-sphere model. The resolution of this paradox (Fisher 1984) is that if all possible terms are included in the LGW Hamiltonian then the t-expansions of ρ_d and δ contain both types of term; that is $(1-\alpha)$ and $(\theta_5 + \beta)$ in ρ_d, as shown previously by Nicoll (1981, equation (5.20*b*)), and $(\mu - \beta - 1)$ and $(\theta_5 - \nu)$ in δ. Presumably it is the hidden symmetry of the penetrable-sphere model that makes the coefficient of the $(\theta_5 - \nu)$ term zero, and leaves only that in $(\mu - \beta - 1)$.

Fisher and Wortis were unable to deduce the behaviour of δ in the critical region ($d=3$) from the ($\theta_5-\nu$) term because of the poor convergence of the ε-expansion of θ_5;

$$\theta_5-\nu=\tfrac{11}{12}\varepsilon-\tfrac{293}{324}\varepsilon^2. \tag{19}$$

The exponent ($\mu-\beta-1$), which is equal to ($1-\alpha-\beta-\nu$), is about -0.06 for $d=3$, and $-\frac{1}{8}$ for $d=2$. Its ε-expansion is

$$\mu-\beta-1=-\tfrac{1}{12}\varepsilon+\tfrac{13}{324}\varepsilon^2. \tag{20}$$

It follows that δ diverges at the critical point at least as rapidly as $|t|^{\mu-\beta-1}$.

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