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Critical Behavior of the Free Surface of Liquid ^{4}He Near the λ Point

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The noncriticality of the free surface of liquid ^{4}He near the λ point and the finite-size scaling postulate are combined to show that the surface tension can have two singularities, one due to rounding and another due to shifting. The rounding singularity can be reduced, via a further scaling assumption, to that previously suggested by Sobyanin and Hohenberg. Results from calculations based on continuous symmetry models and experiments on topologically 2D ^{4}He films are used to argue that the shift singularity is $|t|^{1-\alpha}$, which is consistent with the leading singularity observed by Magerlein and Sanders.

1. INTRODUCTION

The essential role that the continuous symmetry of the order parameter plays in determining the nature of critical phenomena in systems with restricted geometries (see, e.g., Ref. 1) is firmly established. For example, a two-dimensional Ising model with no continuous symmetry displays a critical point below which spontaneous magnetization (long-range order) exists; whereas a two-dimensional planar (xy) model with continuous symmetry exhibits a critical point, but with no spontaneous magnetization at any nonzero temperature.[2] Since the continuous symmetry of the two-component ($n = 2$) vector order parameter of the planar model is equivalent to that of the complex order parameter of superfluid ^{4}He, it is customary to identify superfluid ^{4}He as a physical realization of the planar model. Although this identification has been successful in the bulk, only recently has there been support from experiments[3] on superfluid ^{4}He films for analogous identification in restricted geometries.

The phase transition of the two-dimensional planar model[2] can be attributed to topological excitations, bound vortex–antivortex pairs,

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threading the system normal to the plane of the system. Consequently, the topology of the ^{4}He films is expected to play an important role in the nature of critical phenomena. In particular, superfluid ^{4}He films adsorbed on a substrate with a complicated three-dimensional topology, e.g., porous Vycor glass, show a critical behavior similar to the bulk,[4] whereas ^{4}He films adsorbed on a flat substrate with two-dimensional topology display a distinctive two-dimensional critical behavior.[3,*] To distinguish between these two classes of film critical behavior, we introduce a topological dimension by calling the former *3D films* and the latter *2D films*. It is the 2D film that displays the universal jump in the superfluid density[3] predicted by the two-dimensional planar model.[2]

In the light of these successes in 2D film and bulk critical phenomena in superfluid ^{4}He, we consider in this paper a case that can be interpreted as lying in between the 2D film and bulk: the liquid–gas interface of ^{4}He near the λ point. Precision measurements by Magerlein and Sanders[5,†] of the surface (interfacial) tension σ of the ^{4}He liquid–gas interface at temperatures T near the λ point at T_c yield a critical behavior in disagreement with present theories.[7,8] To be specific, let the leading singularity of σ be $|t|^{\mu}$, where $t=(T-T_c)/T_c$ and μ is the surface tension exponent. The theoretical prediction[7,8] is $\mu=2-\alpha-\nu\approx 1.35$, where α is the specific heat exponent and ν is the correlation length exponent. To obtain this result, Sobyanin[7] uses a Ginzburg–Landau–Pitaevskii model with specific surface boundary conditions, and Hohenberg[8] uses a simple scaling argument in which a surface length is identified with the bulk correlation length of the critical liquid phase. The experimental data[5] are not consistent with this prediction and imply a *stronger* singularity with $\mu\approx 1-\alpha\approx 1.0$.

Thermodynamically the λ point is a critical end point located at the juncture of the λ line with the liquid–gas coexistence curve. Near the λ point, the liquid–gas interface is clearly noncritical (the interfacial thickness does not become arbitrarily large) since the gas phase is noncritical. Widom[9] has investigated phenomenologically the noncritical interface near a critical end point, but only for systems characterized by *one* scalar ($n=1$) order parameter. The theoretical prediction[9] is that σ should have positive slope near the critical end point, $d\sigma/dT>0$. The experimental data[5] show the opposite, $d\sigma/dT<0$.

It is clear that at the present time neither the leading noncritical behavior ($d\sigma/dT$) nor the leading critical behavior ($|t|^{\mu}$) of σ near T_c is understood. The purpose of this paper is to discuss only the critical behavior of σ, exploiting the noncriticality of the liquid–gas interface and finite-size scaling as well as the continuous order-parameter symmetry and the

*In Ref. 3 the helium is adsorbed on a Mylar film substrate, in Ref. 4, on porous Vycor glass.
†Previous and less precise measurements of σ near the lambda point include Refs. 6.

topological dimensions of films. In this regard, it is important to distinguish between the unsubstantiated singularity[7,8] $\mu = 2 - \alpha - \nu$ for a *noncritical* liquid–gas interface of a *vector* ($n = 2$) system with continuous symmetry and the identical but verified singularity[10] for a *critical* liquid–gas interface of a *scalar* ($n = 1$) system with no continuous symmetry.

In Section 2, the noncriticality of the liquid–gas interface near T_c is used to show that the singular surface tension $\tilde{\sigma}$ is a surface correction to the bulk free energy. The finite-size scaling postulate of Fisher[1] is then employed to show that $\tilde{\sigma}$ can have two singularities, one due to rounding and another due to shifting. In other words, finite-size effects can determine $\tilde{\sigma}$. The rounding singularity is reduced in Section 3, via a further scaling assumption, to that suggested previously by Sobyanin[7] and Hohenberg.[8] Results from calculations based on models with continuous symmetry and from experiments on 2D films of superfluid ^{4}He are utilized to argue that the shift singularity might be $|t|^{1-\alpha}$, which dominates the rounding singularity and is consistent with the leading singularity observed by Magerlein and Sanders.[5] A brief discussion follows in Section 4.

2. SURFACE TENSION OF A FREE SURFACE

The interface of interest is one between a noncritical gas phase and a critical liquid phase, which we can call the *free surface* of the liquid. Consider the critical liquid phase to have cross-sectional area A and length L with identical free surfaces on the two ends but periodic boundary conditions on the sides. Let $A \to \infty$ to obtain a 2D film ($\infty \times \infty \times L$) in contact at the two free surfaces with the noncritical gas phase. The length L is then allowed to grow large, resulting in a *thick* 2D film with two free surfaces.

Since the λ point is far from the liquid–gas critical point, the total free energy per unit volume $F(T, L)$ of a thick, 2D film is asymptotically ($L \to \infty$) decomposable into a bulk contribution $F_\infty(T)$ and two surface contributions $\sigma(T)$:

$$F(T, L) = F_\infty(T) + (2/L)\sigma(T) + \cdots \tag{1}$$

where higher order terms which go to zero faster than $1/L$ as $L \to \infty$ are omitted. The *surface tension* $\sigma(T)$, with dimensions energy/area, is assumed to be finite as $A \to \infty$, and the bulk free energy per unit volume $F_\infty(T)$ is finite as $A \to \infty$ and $L \to \infty$. The expansion (1) is obviously not valid near the liquid–gas critical point, where the interfacial thickness becomes arbitrarily large, and in this sense (1) takes into account the noncriticality of the free surface.

The (bulk) liquid phase has a critical point at T_c. Near T_c we can separate thermodynamic quantities into a regular (noncritical) contribution and a singular (critical) contribution. The same decomposition as in (1) is expected to be valid for the singular contribution:

$$\tilde{F}(t, L) = \tilde{F}_\infty(t) + (2/L)\tilde{\sigma}(t) + \cdots \tag{2}$$

where $t = (T - T_c)/T_c$ and the tilde indicates the singular part. To leading order, the noncritical gas phase is eliminated in (2). More importantly, the singular surface tension can be considered as the surface correction to the bulk free energy density.

Having reduced $\tilde{\sigma}$ to a surface correction to the bulk, we employ the basic scaling postulate[1] for the singular free energy density of a thick, 2D film in the form

$$\tilde{F}(t, L) = \tilde{F}_\infty(\dot{t})Q(l|\dot{t}|^{1/\theta}) \tag{3}$$

where $\dot{t} = [T - T_c(l)]/T_c = t + t_c(l)$ is the shifted temperature deviation, and $t_c(l) = bl^{-\lambda}$ is the shift from T_c in $T_c(l)$ of a thick ($l \to \infty$), 2D film. Here Q is a dimensionless scaling function and the dimensionless $l = L/a$ is the thickness L in terms of a microscopic spacing a. Equation (3) summarizes the two finite-size effects: in a thick film the critical point is shifted to $T_c(l)$ with shift exponent λ and rounded with rounding exponent θ. The scaling postulate (3) has been verified by detailed calculations on the spherical model[11] and on the ideal Bose gas,[12,13] by the renormalization-group method,[14] and by specific heat measurements on superfluid ^{4}He films.[15,*]

Let us specialize (3) to surface corrections to the bulk.[1] To recover the bulk, $Q(\infty)$ must be set equal to one. To obtain surface corrections to the bulk, $Q(Z)$ must have an asymptotic ($Z \to \infty$) expansion

$$Q(Z) = 1 + cZ^{-1} + \cdots \tag{4}$$

It follows from Eqs. (2)–(4) that the singular surface tension can have two contributions:

$$\begin{aligned} \tilde{\sigma}(t) &= \tilde{\sigma}_s(t) + \tilde{\sigma}_r(t) \\ &= abl^{1-\lambda}\tilde{F}'_\infty(t) + ac|t|^{-1/\theta}\tilde{F}_\infty(t) \end{aligned} \tag{5}$$

where $\tilde{F}'_\infty = d\tilde{F}_\infty(t)/dt$. The first term $\tilde{\sigma}_s$ is due to shifting, and the second term $\tilde{\sigma}_r$ is due to rounding. Note that, depending on the value of λ, the shift singularity $\tilde{\sigma}_s$ may not exist or may be weakly size-dependent, whereas the rounding singularity $\tilde{\sigma}_r$ always exists and is size-independent.

Equation (5) shows that, even though L is large, finite-size effects can determine the singularities in $\tilde{\sigma}$. The underlying assumption can be traced back to Eq. (1) and to the noncriticality of the free surface, viz., that the structure of the free surface can be neglected. This assumption is certainly

*In Ref. 15 the helium is confined in Nuclepore filters.

wrong near the liquid–gas critical point, where the interface becomes arbitrarily thick, but is reasonable far from the liquid–gas critical point, as at the λ point T_c. There is, however, a reservation. At T_c the density profile is asymmetric[9] and may approach the density of the critical liquid phase as a power law rather than an exponential. If the power-law density profile is verified, the above analysis may have to be modified.

3. SHIFT AND ROUNDING SINGULARITIES

To obtain an explicit form of $\tilde{\sigma}_r$, we write $\tilde{F}_\infty$ in its standard form

$$\tilde{F}_\infty(t) = A_\infty t^{2-\alpha}(1 + D_\infty t^x + \cdots), \qquad t > 0 \tag{6}$$

where a similar expression holds for $t < 0$, and x is the confluent exponent. It follows from (5) and (6) that the rounding singularity has the form

$$\tilde{\sigma}_r(t) = \tilde{\sigma}_{r0} t^{2-\alpha-1/\theta}(1 + D_\infty t^x + \cdots), \qquad t > 0 \tag{7}$$

where the coefficient is given by $\tilde{\sigma}_{r0} = acA_\infty$. The rounding exponent $1/\theta$ is defined in (3) as a thermodynamic crossover exponent and is not expected to be strongly affected by the topological connectiveness of the film. In other words, it is probably safe to take θ from measurements[15] on 3D ^{4}He films, which gives $1/\theta \approx 0.54$ and a leading rounding singularity $|t|^{1.48}$. If we make the further scaling assumption that rounding occurs when the bulk correlation length $\xi = \xi_0 t^{-\nu}$ is comparable to L, then we get the bulk value $\theta = 1/\nu$ and a leading rounding singularity $|t|^{2-\alpha-\nu}$, which is the same as that suggested by Sobyanin[7] and Hohenberg.[8] If the usual value of ν is assumed ($\nu \approx 0.67$), then the leading rounding singularity is $|t|^{1.35}$, which is stronger than $|t|^{1.48}$ but still inconsistent with the leading singularity observed by Magerlein and Sanders.[5]

To obtain an explicit form of $\tilde{\sigma}_s$, we need in addition to (6) a particular value of the shift exponent λ. The shifted $T_c(l)$ can be identified with the onset of superfluidity of a thick, 2D film, which is given for small l by the two-dimensional planar model.[2] Therefore, as mentioned in the introduction, the continuous symmetry of the $n = 2$ order parameter and the 2D topology of the thick film are expected to play important roles in the critical behavior, in particular in determining $T_c(l)$ and λ. In lieu of a calculation of λ in a thick, 2D, planar-model film or a measurement of λ in a thick, experimentally verified 2D, ^{4}He film, we turn to other calculations and experiments that satisfy the selection rules of continuous symmetry and 2D topology.

Theoretically, the problem is not with the 2D topology but with the nature of the continuous symmetry as parametrized by n. A relevant calculation was made by Doniach,[16] who calculated $T_c(l)$ for a thick, 2D, large-n film and extrapolated to $n = 2$. The result was $\lambda = 1$. Series expansion calculations on a 2D Heisenberg ($n = 3$) film[17,*] yielded $\lambda = 1.1$, which is not inconsistent with $\lambda = 1$ for $n = 2$. (It is unclear how these results can be harmonized with the zero transition temperature of two-dimensional systems with $n > 2$.) Fisher[1] has emphasized that in the presence of a constraint, such as constant density, $\lambda = 1$. If $\lambda \approx 1$, then $\lambda < \theta$, i.e., the shift is asymptotically larger than the rounding. Both of these points, $\lambda = 1$ and $\lambda < \theta$, are corroborated by detailed calculations on the ($n = \infty$) spherical model[11] and ideal Bose gas.[12] Admittedly, none of the estimates appears to be compelling.

Experimentally, the problem is not with the continuous symmetry (superfluid ^4He is always $n = 2$), but with the 2D topology. The specific heat measurements of multilayer ^4He by Bretz[20,†] have been analyzed by Doniach,[16] who found agreement with $\lambda = 1$. The result $\lambda = 1$ is, however, in marked disagreement with the $\lambda \approx 3/2$ bulk behavior found in other measurements‡ on superfluid ^4He in restricted geometries. [The bulk result $\lambda = 1/\nu \approx 3/2$ can be obtained by insisting that the shifted $T_c(l)$ occurs when the bulk correlation length $\xi = \xi_0 t^{-\nu}$ is comparable to the thickness L.] We can attribute this difference to a change in topological dimension, viz., from the 2D film on a flat substrate[3,20] to the 3D film on a porous medium.[4,21] It is certainly possible that part of a ^4He film is 2D and part is 3D or that the topological dimension is between 2 and 3, either of which would blur the above distinction between 2D and 3D films.

To summarize, the selection rules of continuous symmetry and 2D topology have suggested the possibility $\lambda \approx 1$, based on theoretical estimates[16,17] on continuous symmetry models of 2D films and experimental measurements[20] on superfluid ^4He films, presumably 2D, absorbed on a flat substrate.

Accepting the suggested 2D, $n = 2$ result $\lambda = 1$, we find that the shift singularity has the form

$$\tilde{\sigma}_s(t) = \tilde{\sigma}_{s0} t^{1-\alpha}(1 + D_{s\infty} t^x + \cdots), \qquad t > 0 \tag{8}$$

where the coefficients are given by $\tilde{\sigma}_{s0} = ab(2-\alpha)A_\infty$ and $D_{s\infty} = D_\infty(2-\alpha+x)/(2-\alpha)$. Note that $\tilde{\sigma}_s$ is size-independent only if $\lambda = 1$ exactly. However, λ need not be exactly unity in order for $\tilde{\sigma}_s$ to exist. (If $L \approx 1$ cm, $a \approx 1$ Å, then an exponent $\lambda = 1.06$ would decrease the shift contribution relative to that for $\lambda = 1$ by a factor of $l^{1-\lambda} \approx 0.3$.) Of course, in such a case, $\tilde{\sigma}_s$ would be weakly size-dependent.

Comparing (8) with (7), we see that for an acceptable range of θ (e.g., $0.54 \leqslant 1/\theta \leqslant 0.67$) the shift singularity (8) dominates the rounding

*Measurements of the electrical resistivity of Ni films, see Ref. 18, yield $\lambda = 1.01 \pm 0.10$, which is consistent with $\lambda \approx 1$ or with the suggestion in Ref. 19 that $\lambda = 1 + \eta$.

†In Ref. 20 the helium is adsorbed on an exfoliated graphite substrate.

‡See, e.g., Ref. 21, where $\lambda = 1.54$ is found for helium in porous filters.

singularity (7). Furthermore, $\mu = 1 - \alpha$ from (8) is consistent with the leading singularity found experimentally by Magerlein and Sanders.[5]

4. DISCUSSION

The main result is that the singular surface tension $\tilde{\sigma}$ can have two singularities at T_c, one due to rounding and another due to shifting, that are distinctive of finite-size scaling. The argument that the shift singularity $\tilde{\sigma}_s$ is given by $|t|^{1-\alpha}$, which dominates the confluent rounding singularity $|t|^{2-\alpha\ \ \nu}$, is tentative and is based on the suggestion $\lambda \approx 1$.

Direct evidence for or against $\lambda \approx 1$ awaits measurements of the onset temperatures in experimentally verified 2D films[3] of superfluid ^{4}He. An experimental signature of a 2D film is excess dissipation only in the immediate vicinity of $T_c(l)$. In other words, the measurement of $T_c(l)$ needs to be accompanied by a measurement of the presence or absence of excess dissipation near $T_c(l)$. Such a measurement of λ would clarify the role of topology on the film critical behavior. Alternatively, measurement of the size dependence of $\tilde{\sigma}$ can be used to obtain some information about λ. For example, if the leading singularity of $\tilde{\sigma}$ is found to be $|t|^{1-\alpha}$ *and* independent of l, then one could conclude that $\lambda = 1$. If the leading singularity of $\tilde{\sigma}$ is weakly l-independent, then $\lambda \approx 1$ and can be so determined. In either case the thickness L must be precisely measured.

In the meantime, it is instructive to compare the precision measurements of σ by Magerlein and Sanders[5] with the precision measurements of the density ρ by Van Degrift.[22] In both cases there is a leading $|t|^{1-\alpha}$ singularity at T_c and, upon closer scrutiny, an additional feature near but not at T_c. In σ the point of maximum curvature is seen to occur slightly (~mK) below T_c, whereas in ρ the maximum itself occurs slightly (~mK) above T_c. The point here is that this additional feature near T_c in σ, as is the case in ρ,[22] is not to be considered as a critical phenomenon,[5] but is to be attributed to the interplay between the regular contributions to σ and the confluent singular contributions $\tilde{\sigma}$. In other words, the only critical phenomenon in σ occurs at T_c and other features involve the nonsingular part of σ.

The remaining feature in σ that is not qualitatively understood is the nonsingular feature of a negative slope, $d\sigma/dT < 0$, in direct contradiction to the positive slope predicted by a one scalar order-parameter model.[9] The complicated two-order-parameter models may provide the essential clue.

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