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Corrections to scaling and surface specific heat of confined helium

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In earlier work by Chen and Gasparini it was found that leading-order finite-size scaling for the specific heat of helium confined to films and pores did not seem to hold. We present here an analysis which includes correction-to-scaling terms. We do this in two ways: First, we use equations for the shift and value of the specific-heat maximum as suggested by Fisher. Secondly, we show that a bulk-plus-surface specific-heat model yields very similar equations for the shift and maximum, and in addition suggests a simple power law for the scaling function near T_λ. All aspects of the data can be fitted very simply with this model with only three parameters. We find, however, that the surface specific-heat exponent α_s does not agree with the scaling prediction $\alpha_s = \alpha + \nu$. When correction-to-scaling terms are introduced to force agreement, we find these terms to be very large, larger than the leading terms, and several orders of magnitude larger than the equivalent correction-to-scaling amplitudes for bulk helium. We believe our analysis in terms of the surface specific heat is the first for an experimental system, and we find that it is quite in keeping with the spirit of some theoretical calculations.

I. INTRODUCTION

Physical systems near a phase transition have a marked dependence on dimensionality. This can be explored experimentally with samples where one of the physical dimensions becomes comparable to that of the correlation length. Practically this might mean film samples whose thickness is in the range of one to perhaps 1000 atomic layers. For a fixed film thickness, and as a function of temperature, one might expect that far away from the transition the response of the system would not be much affected by its finite extent. As one approaches the transition temperature, T_c, and the correlation length increases, one expects deviations from bulk behavior, and eventual crossover into a two-dimensional regime. If one measures a thermodynamic response such as the heat capacity, which might display a sharp cusp or a divergence in the bulk system, then one would expect a rounded maximum at some temperature T_m, typically below T_c. One might expect,[1] in the most simple case, that the dependence of T_m on say the film thickness, d, be given by a power law,

$$(T_c - T_m)/T_c \equiv t_m = a_0 d^{-\Lambda} \ . \tag{1}$$

Further, on the simple argument that the maximum is associated with the bulk correlation length, ξ, becoming of the order of d, one might conjecture[1]

$$\Lambda = 1/\nu \ , \tag{2}$$

where ν is the exponent which characterizes the divergence of ξ. The constant a_0 will depend on geometry and boundary conditions. More generally one expects correction-to-scaling terms to contribute, and Eq. (1) to read[2]

$$t_m = a_0 d^{-1/\nu}(1 + a_1 d^{-\omega/\nu} + a_2 d^{-(2\nu+1)/\nu} + \cdots) \ , \tag{3}$$

where ω is the correction-to-scaling exponent, and $\Lambda = 1/\nu$ has been assumed.

Also, in the case of the heat capacity, the maximum value, C_m, that is achieved at t_m is expected to leading order to be[1]

$$C_m = A\,\theta \ln d + \text{const} \ , \tag{4}$$

where according to scaling

$$\theta = 1/\nu \ . \tag{5}$$

Equation (4) applies if the bulk system has a logarithmic divergence with amplitude A. If the bulk heat capacity has a characteristic exponent $\alpha \neq 0$, then likely corrections to Eq. (4) will be of order α. In addition, just as in the case of the shift, one expects corrections-to-scaling terms, hence more generally,[2] but still for $\alpha = 0$,

$$C_m = A/\nu \ln d + B + B_1 d^{-\omega/\nu} + B_2 d^{-1} + \cdots \ , \tag{6}$$

where the constants B's are expected to be geometry and boundary conditions dependent.

Equations (3) and (6) apply to the particular temperature at which the heat capacity achieves a maximum. More generally however, one expects that in the critical region near T_c the heat capacity of the finite system would scale as a function of dt^ν, where $t \equiv |1 - T/T_c|$.[1] The functional form is not known from theory, neither are the corrections-to-scaling terms.

Liquid helium near the superfluid transition is an ideal system to study finite size effects because of its ability to form thick films on surfaces in contact with it. The substrate upon which the helium film forms plays an inert role at the transition in the sense that the pressure which results from the van der Waals attraction does not affect the critical behavior of the order parameter. This does not mean, however, that the substrate plays no role: in the case of Grafoil it has been suggested that for thickness of ~3 to 18 layers the films are unstable toward droplets formation thus giving an inhomogeneous confining geometry.[3] In the case of Vycor glass the geometry of the substrate is such that to apparently induce three-dimensional-like behavior even in films less than a monolayer thick.[4]

Many measurements of heat capacity for films of helium, or for helium confined to small dimensions have demonstrated *qualitatively* the finite size behavior discussed above.[5–10] It has not been possible until recently, however, to test *quantitatively* the theoretical predictions.[11] One of the major difficulties had been the lack of uniformity in confinement. In the case of films, one runs into difficulties with capillary condensation. This is especially true if one attempts to measure films thicker than ~10 Å and employs fine packed powders as the substrate. Even in the case of Grafoil, a most ideal substrate for studies of films of the order of 1 or 2 layers, the data for thicker films suggest capillary condensation[9] in addition to, or perhaps as an alternate to the mechanism of droplet formation.[3] In the case of complete confinement, i.e., helium filling a region of space of the order of ~1000 Å, the problem of uniformity is even more acute. Packed powders are clearly not a solution.

In the work of Chen and Gasparini,[9,11,12] Nuclepore filters were used as the confining medium to measure the heat capacity of both films of helium and helium filling the pores of the filters. These data afforded for the first time a test of finite-size scaling for the specific-heat maximum and temperature shift.[11] These were also the first data to show scaling above and below the transition, in the neighborhood $t \lesssim 10^{-2}$. It was found, however, that while the data could be described by the leading scaling forms, Eqs. (1), (4), the scaling exponent was not $1/\nu = 1/0.675$,[13] but rather ~1/0.54.[11]

In this paper we undertake a further analysis of these data in an attempt to understand this discrepancy. Specifically, we explore the possibility that correction-to-scaling terms account for the difference. We also analyze the data from the point of view of a bulk-plus-surface specific heat, the latter characterized by an exponent α_s. We show that this is a useful way to look at the data and that it suggests very simple scaling functions near the transition.

We can summarize the results of our work as follows: No aspects of the specific heat of confined helium, the shift, the maximum, or the scaling near T_λ, agree with leading-order correlation-length scaling. When corrections terms are introduced to force agreement, their amplitude is larger than the leading term, and several orders of magnitude larger than equivalent terms for bulk helium. In the case of the bulk-plus-surface analysis, we find that all aspects of the data can be characterized very simply by only three parameters. In particular we find $\alpha_s(T < T_\lambda) = \alpha_s(T > T_\lambda)$, i.e., scaling between surface exponents; but, $\alpha_s \neq \alpha + \nu$, i.e., failure of scaling among bulk and surfaces exponents. One possible conclusion from the results is that if one is unwilling to accept these large correction-to-scaling terms, then it would seem that the presence of confining surfaces manifests a new critical length.

The remainder of this paper is organized as follows: We first discuss some of the more relevant experimental details, and then briefly the results of the analysis of Ref. 11. We extend this analysis to include correction-to-scaling terms, and then present an analysis in terms of the surface free energy. This is followed by a section where we comment on relevant experimental results for helium and other systems, as well as some theoretical results. Section VII is our summary and conclusions. In an Appendix we discuss a model for the effect on the heat capacity of the films due to the pressure gradient from the van der Waals attraction.

II. EXPERIMENTAL DETAILS

The data we will be analyzing are for films of helium formed on Nuclepore[14] filters of nominal pore diameter of 2000 Å; and data for helium filling pores of diameter 2000, 1000, 800, and 300 Å. Various aspects of the measurements have been published previously,[9–12] and only the more relevant, and some additional details will be mentioned here. The filters were chosen as a substrate as opposed to other possible methods of confinement, because of the relative uniformity of the pore size. For instance, a study of electron micrographs of the 2000-Å filters shows that better than 80% of the helium filling the pores would be within 10% of the mean diameter.[15] This diameter is less than the nominal, manufacturer value by about 10–20%.[14] This is not a serious factor and agrees with the manufacturer's specifications that the nominal size reflects more correctly the upper bound rather than the mean. In our own use of the filters only the relative size is important, and not the absolute value.

The calorimeter, of a similar design as used previously,[16] contained several hundred filters. They are 47 mm in diameter and 5 or 10 μm thick. They were packed with an average separation of 10–20 μm with no attempt to achieve uniform spacing. As it turns out, there is a natural tendency for the filters to keep apart due to electrostatic charges. Measurements of adsorption isotherms with both helium and nitrogen established that there is no dependence on manufacturer's batch, i.e., 1st and 2nd layer completion on samples of 50 to 2000 filters was found strictly proportional to the number of filters.[12] From the helium isotherms it was shown that the determined adsorption area was consistent with N_2 adsorption if the density of the second layer was equal to the density of bulk liquid. The first layer behaved as a 2D solid with a T^2 heat capacity. The number of moles to form this first layer, of thickness ~3 Å, was subtracted in later analysis when the liquid film thickness is needed. Although we formally proceeded in this manner none of our conclusions depend on this procedure. Indeed, in the case of the filled pores, this first solid layer is totally irrelevant.

From the adsorption isotherms we also determined the van der Waals constant which was found to agree with a theoretical estimate. This was an important result, because it allowed us to calculate the limiting film thickness before a uniform film of helium would capillary condense in the pores.[17] This agreed with the experimental determination of this condensation for the filters of 2000-Å size. In Fig. 1 we show this result. These are specific-heat data for which various amounts of helium are condensed in the calorimeter. We see that as the number of moles condensed increases a peak begins to develop near T_λ which is dis-

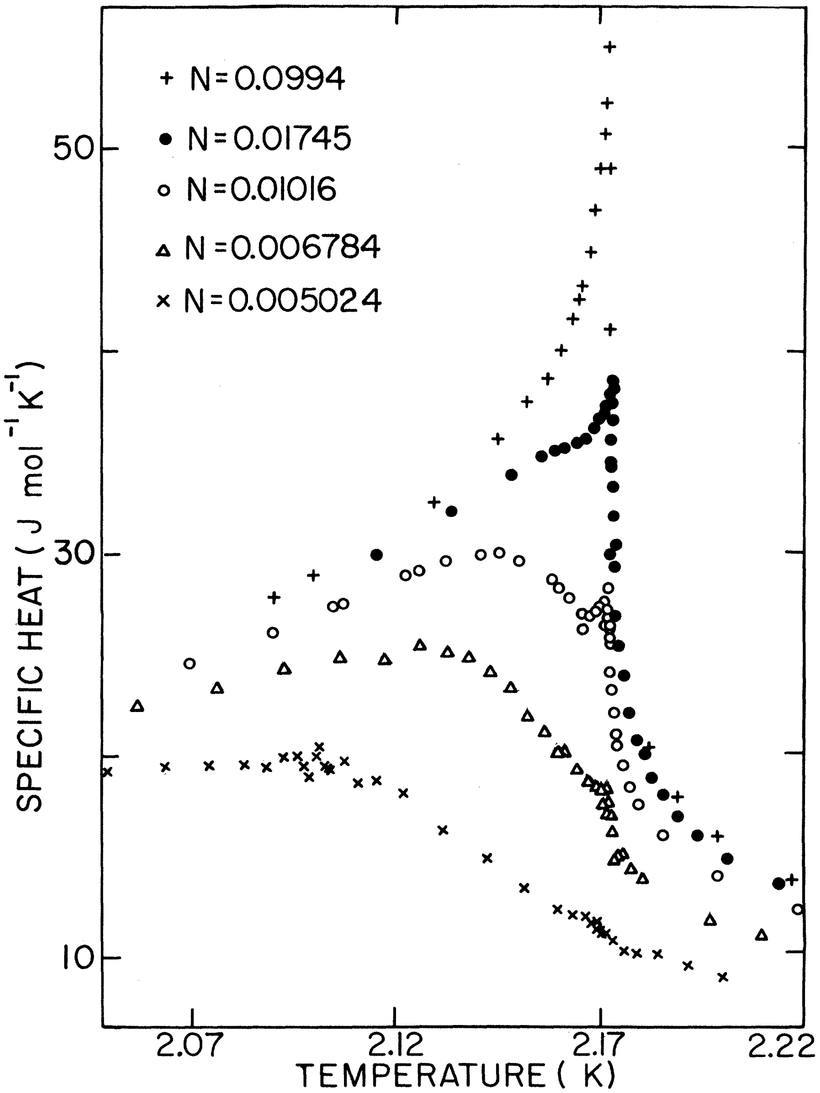

FIG. 1. Specific heat of various amounts, moles, of helium condensed in a calorimeter containing filters of 2000-Å pore diameter. The peak near 2.172 K is a signature of the helium beginning to fill the pores.

tinct from a low-temperature maximum. This peak is the result of a capillary condensed phase with a characteristic confinement of the pore diameter. The low-temperature maximum is due to the film, 56-Å thick, in equilibrium with the condensed phase. The total heat capacity is, of course, a convolution of these two effects. All the data on films which we will be discussing are for film thicknesses smaller than the limit for capillary condensation.

The specific heat of the films was obtained from the measurments of total heat capacity by first subtracting the empty cell contribution, and then correcting for the vapor. We used the following expression,[18]

$$n_l C_{Pl} = C + 2T\frac{\partial v_l}{\partial T}\bigg|_P \frac{dP}{dT} + T\frac{\partial v_l}{\partial P}\bigg|_T \left(\frac{dP}{dT}\right)^2 - n_v C_{Pv} + 2T\frac{\partial v_v}{\partial T}\bigg|_P \frac{dP}{dT} + T\frac{\partial v_v}{\partial P}\bigg|_T \left(\frac{dP}{dT}\right)^2 , \quad (7)$$

where C's are the heat capacities, n the number of moles, and v molar volume. The subscripts v and l refer to liquid and vapor. In practice the terms involving v_l can be ignored to an accuracy of better than 0.1%. The terms involving v_v have to be evaluated carefully and contribute as much as 70% of the heat capacity in the region of the specific-heat maximum. The procedure we followed was to measure the vapor pressure as function of temperature for each film. We found that a reasonable approximation in the region of the specific-heat maximum is to take $P = fP_0$, where P_0 is the saturated vapor pressure, and f varied between 0.96 and 0.34 for the range of films we measured.[19] This procedure is not strictly correct, but is adequate for our data. Most importantly we found that the position (but not the magnitude!) of the specific-heat maximum is not affected at all by this analysis. We further note that the use of Eq. (7) does not correct the data to a path of constant film thickness. The actual thickness we will need and use will be the value for the films at the position of the maximum.

In the case of the helium completely filling the pores of the filters, the correction due to the vapor are much smaller, typically a few percent. The procedure we followed in this case was to condense just enough, or slightly less helium than required to fill the pores. This results in some degree of inhomogeneity in confining dimension because of the film of helium present on the flat surfaces of the filters. This effect is hard to estimate; however, if the films on the flat portions are equal to the metastable thickness of the film in equilibrium with the filled pores, then the amount is small. It is about 3×10^{-4} mol, which is less than 1% of the amount in the pores in all cases except in that of the 300-Å filters where it is ~5%. Some of these facts, and other relevant parameters of the calorimeter are presented in Table I.

One of the important determinations in our study is the shift in the transition temperature, or better the position of the specific-heat maximum. The procedure we followed was to establish the transition temperature T_λ for a bulk sample of helium (~1 cm^3) which had been condensed in the needle valve space outside the volume of the calorimeter containing the filters. This determination was done by drifting slowly through the transition and observing a sharp break in the warming rate at T_λ. The needle valve was then opened, and helium allowed to fill the pores of the filters. We found that even upon recycling the cryostat to change the filters for different runs, T_λ did not change by more than ~80 μK. A summary of specific-heat maximum and temperature shift for films and pores is given in Table II.

We also measured the heat capacity of bulk helium to check on our procedures. We found excellent

TABLE I. Some physical characteristics of the calorimeter. All the filters used have a diameter of 47 mm.

Pore diameter[a] (Å)	Filter thickness[a] (μm)	Number of filters used	Area per filter[b] (cm^2)	Moles in calorimeter Total	Vapor (10^{-4})	1st layer
2000	10	450	546 ± 33	792	1.63	4.73
1000	5	666	289 ± 6	401	2.35	3.51
800	5	693	432 ± 8	377	5.29	5.55
300	5	630	273 ± 16	66.8	8.21	2.93

[a] Manufacturer specification, see Ref. 14.

[b] Obtained by assigning 15 Å per N_2 molecule, see Ref. 12.

TABLE II. The shift of the temperature of the specific-heat maximum and its value for various confining dimensions. In the case of the films the thickness is that above the first layer. In the case of the filled pores, the size is the diameter as given by the manufacturer.

Film (Å)	Pore (Å)	$T_\lambda - T_m$ (K)	Specific-heat maximum (J/mol K)
10.1[a]		0.569 ±0.03	7.6 ±0.2
17.2		0.425 ±0.02	13.2 ±0.2
25.0		0.202 ±0.02	17.5 ±0.5
32.8		0.126 ±0.01	20.1 ±0.2
37.9		0.102 ±0.005	21.4 ±0.7
42.2		0.075 ±0.005	22.9 ±0.6
53.0		0.050 ±0.004	26.1 ±0.6
	300	0.0062 ±0.001	37.4 ±0.5
	800	0.001 20 ±0.0001	48.0 ±1
	1000	0.000 80 ±0.0001	49.5 ±1
	2000	0.000 23 ±0.000 03	56.4 ±1

[a] Data for this thickness fall outside the applicability of Eqs. (1) and (4) and are not used in the analysis.

agreement with earlier results,[20–22] and no systematic errors. These data for bulk helium were also used in later analysis where the difference between bulk and confined specific heat was needed.

III. LEADING-ORDER ANALYSIS

An analysis of the data in which only leading-order terms were used was done by Chen and Gasparini.[11] Their results are listed in Table III. They found that $\Lambda \simeq \theta \neq 1/\nu$. Further they noticed that both films and pores gave consistent results and could be analyzed together by empirically assigning a thickness d to the pore data of diameter D, such that $d = 0.585D$. The result of this analysis is also shown in Table III. The fact that the films and pores data give consistent results is an important check on the experiment since the two types of data could be subject to quite different systematic errors.

In addition, they tested the data in the neighborhood of T_λ, $t \lesssim 10^{-2}$, with the following equation

$$[C(t,d) - C(t,\infty)]t^{\alpha} = g(d^{\theta}t) - g(\infty) \ , \tag{8}$$

where α is the bulk specific-heat exponent, $g(\infty)$ is a constant, and the C's are the specific heats of the confined and bulk helium. They found that while the

TABLE III. Results of fitting the specific heat to expressions without corrections to scaling.

	Shift $1/\Lambda$	Maximum $1/\theta$	Scaling function $1/\theta$	Equations
Films	0.528 ±0.043	0.466 ±0.015	· · ·	(1),(4)
Pores	0.583 ±0.046	0.502 ±0.025	· · ·	(1),(4)
Pores and films; $\alpha = 0$	0.562 ±0.014	0.489 ±0.013	· · ·	(1),(4)
Pores and films; $\alpha \neq 0$, $1/\theta = \alpha_s - \alpha$		0.546 ±0.007	0.54(±0.02)	(16),(8)

data did scale this way, the best exponent was not $1/\theta = \nu = 0.675$, but $1/\theta \simeq 0.54$. The error associated with the value of θ could not be established in the sense of a standard error because of the lack of an explicit form for the scaling function $g(d^{\theta}t)$. A reasonable error might be ± 0.02; but, irrespective of this, the scaling definitely favored $1/\theta \neq \nu$.

The conclusion from this work is that while the data could be well described by Eqs. (1), (4), and (8), the expected scaling with the correlation length exponent ν did not seem to hold.

IV. ANALYSIS WITH CORRECTIONS TO SCALING

To check if the deviations from the predicted exponents can be ascribed to correction-to-scaling terms, we have analyzed the shift and maximum data according to Eqs. (3) and (6). The films and pore data are analyzed separately, since the coefficients of the correction to scaling terms can have a rather more complicated dependence on geometry than the simple empirical relation used in the leading order analysis. Since our data are not precise, or extensive enough to yield both ω and the prefactors in Eqs. (3) and (6), the way we proceeded is to assume that the exponent ω is known; we have used $\omega = 0.5$.[23] The goal of the analysis then is to see first of all if the data can be fitted this way and secondly if the amplitudes of the correction terms are "reasonable." Again, there is no theoretical guidance as to their magnitude or even sign. Equation (3) can be written as

$$t_m d^{1/0.675} = a_0 + a_0 a_1 d^{-0.74} + a_0 a_2 d^{-3.5} \ , \qquad (9)$$

and Eq. (6) as

$$C_m - 7.6 \ln d = B_0 + B_1 d^{-0.74} + B_2 d^{-1} \ . \qquad (10)$$

We have used $\nu = 0.675$, and $A = 11.7$ J/mol K as the amplitude of the nearly logarithmic divergence of the bulk specific heat for $T < T_\lambda$. We ignore for the moment the fact that the bulk specific heat cannot be described by a logarithmic divergence in a way consistent with scaling.[16,21,22,24] This effect is small for our present considerations. A more proper analysis for $\alpha \neq 0$ will be done later.

In using Eq. (9) we assume that the term proportional to $d^{-3.5}$ is small, and in Eq. (10) we "absorb" the d^{-1} dependence in the $d^{-0.74}$ term. This is equivalent to saying that a difference of 0.26 in the power dependence of these correction terms cannot be picked up by our data. With these considerations, Eqs. (9) and (10) suggest that a plot of the left-hand side vs $d^{-0.74}$ will yield straight lines whose slope will

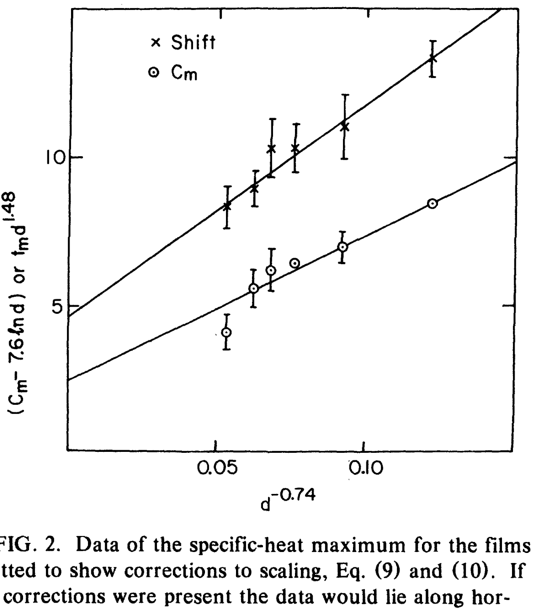

FIG. 2. Data of the specific-heat maximum for the films plotted to show corrections to scaling, Eq. (9) and (10). If no corrections were present the data would lie along horizontal lines. The variable d is the film thickness in angstroms.

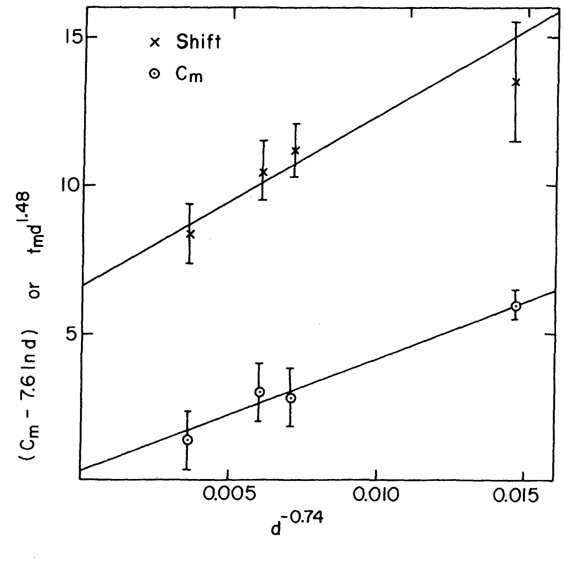

FIG. 3. Data of the specific-heat maximum for the filled pores plotted to show corrections to scaling, Eq. (9) and (10). If no corrections were present the data would lie along horizontal lines. The variable d is the pore diameter in angstroms.

TABLE IV. Results of fitting the specific heat to expressions with corrections to scaling, Eqs. (9), (10), and (12). The errors for the shift and maximum are not statistical but reflect the results of taking the exponent $\omega = 0.5 \pm 0.1$. The confining dimension is in Å, either the film thickness or the pore diameter.

	Shift		Maximum		Equation
	a_0	a_1	B_0 ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	B_1	
Films	4.7 (+0.6,−1.7)	70 (+30,−15)	2.5 (+0.9−1.7)	49 (+13−8)	(9)
Pores	6.6 (+0.9,−1.5)	580 (+800−280)	0.4 (+0.6−1.0)	380 (+420−200)	(10)

	Scaling function			
	b ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	b_1	b_2 ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	
$T < T_\lambda$	-25.2 ± 1.0	20.1 ± 2.0	~ 0	(12)
$T > T_\lambda$	-11.9 ± 0.7	31.3 ± 4.4	-18 ± 13	(12)

give the correction to scaling amplitude. This analysis is shown in Fig. 2 for the films and Fig. 3 for the pores. Clearly, within the errors, the data are consistent with the analysis. The precision of the data and the method of analysis do not warrant a least-squares fit, rather what we have done is to test the sensitivity of the results to variations of the correction to scaling exponent ω. These results are listed in Table IV.

We see from Table IV that the correction terms for both films and pores are large. For $\omega = 0.5$, we have, respectively, $a_1 = 70$, 580 and $B_1 = 49$, 380 J/mol K. These are one to two orders of magnitude larger than the leading terms. To get another perspective on these results, we note that in the case of the bulk specific heat, which can be described by

$$C = (A/\alpha t^{-\alpha})(1 + Dt^{\omega}) + B \ , \tag{11}$$

one finds that to achieve agreement with the scaling prediction of $\alpha = \alpha'$ the correction term is $D \simeq -0.012$.[24] Also, in the case of thermal expansion, which has the same singularity as the heat capacity, one finds by extrapolating to zero pressure that $D \simeq -0.02$.[25] By these measures the corrections to scaling in the case of finite-size effects is very large indeed, three to four orders of magnitude larger!

The next question we address is whether all of the data close to T_λ can be scaled with the correlation length exponent ν plus the addition of correction terms. The following form for the scaling function suggests itself from considerations in the next section:

$$[C(t,d) - C(t,\infty)]d = bt^{-\nu+\alpha}(1 + b_1 t^{\omega}) + b_2 \ . \tag{12}$$

The range of validity of Eq. (12) is expected to be limited to not being too close to T_λ so that $\xi \lesssim d$, and not too far so as to be away from the critical region, i.e., $T \lesssim 10^{-2}$. A more complete discussion of Eq. (12) will be done in the next section. By using $\omega = 0.5$, $\nu = 0.675$, and $\alpha = -0.02$,[24,25] the parameters b, b_1, b_2 were least-squares adjusted to achieve a fit to the left-hand side of Eq. (12). The data were fitted well by this equation, as will be seen more explicitly in the next section. The results for the parameters are presented in Table IV. For the correction terms, b_1's we have 20.1 ± 2.0 for $T < T_\lambda$ and 31.3 ± 4.4 for $T > T_\lambda$. These are obviously much larger than 1, and very much larger than what is encountered in the case of the bulk.

We conclude from the work in this section that to retain a description of finite-size effects as being governed to leading order by the correlation length exponent, one needs to introduce very large—three to four orders of magnitude larger than in the bulk case—correction terms. This is true for the position, and value of the specific-heat maximum for both helium films and helium confined to pores. This conclusion is also strongly supported—to the extent that we can justify Eq. (12)—by scaling of the data in a neighborhood above and below T_λ.

V. ANALYSIS IN TERMS OF A SURFACE SPECIFIC HEAT

One may describe the thermodynamics of a finite system in terms of a total free energy which is the sum of a bulk part, F_∞, and a surface part, F_s,[1,26]

$$F \cong NF_\infty + N_sF_s \ , \tag{13}$$

where N is the total number of particles and N_s is the number at the surfaces. Near a phase transition the validity of this equation is limited to a neighborhood in temperature such that the correlation length ξ is less than, or perhaps of the order of, the smallest sample dimension. The usefulness of Eq. (13) in the present context is that it allows us to derive expressions for the shift and magnitude of the specific-heat maximum as well as—and this is important—a form for the scaling function. This can be done, as we will see, with a great deal of economy in terms of bulk and surface specific-heat parameters. One can also introduce a scaling assumption as well as correction-to-scaling terms in the spirit of the previous section. Another virtue of an approach via Eq. (13), is that whether analyzing the specific-heat maximum, or the data near the transition, the same parameters appear. Thus one can check that the results obtained are consistent. This might not seem significant, since all the equations, as we will see, stem from Eq. (13). However, the range of applicability near T_λ of the scaling function is limited to $t \lesssim 10^{-2}$. This range does not encompass the temperature of the maximum for the films. Thus the maximum in this case gives independent, but not new information. The reason for the different range of applicability is presumably that the scaling function for the specific heat involves two derivatives of the free energy while the specific-heat maximum involves three derivatives. Lastly, the advantage of Eq. (13) is that it will give expressions for $\alpha \neq 0$ which are particularly useful in analyzing the maximum.

We now proceed as follows: We assume a power law dependence for the bulk and surface specific heats, i.e., for the bulk Eq. (11) and for the surface[27]

$$C_s = (A_s/\alpha_s t^{-\alpha_s})(1 + D_s t^{\omega}) + B_s \ . \tag{14}$$

We consider now a film of $\sim\infty$ lateral extent, in which case N/N_s is $\frac{1}{2}$ the number of layers. For helium, with 3.56 Å/layer, $N_s/N = 7.12/d$ where d is in angstroms. From Eq. (13), by setting $d^3F/dT^3 = 0$ we obtain that the position of the maximum, t_m is given by

$$t_m \cong \left(-\frac{7.12A_s}{Ad}\right)^{1/(\alpha_s-\alpha)}\left[1 + \frac{1}{\alpha_s-\alpha}\left(\frac{\omega-\alpha}{\alpha}D - \frac{\omega-\alpha_s}{\alpha_s}D_s\right)\left(-\frac{7.12A_s}{Ad}\right)^{\omega/(\alpha_s-\alpha)}\right] \ . \tag{15}$$

And, for the maximum we obtain

$$C_m \cong A\left(\frac{\alpha_s-\alpha}{\alpha_s\alpha}\right)\left(-\frac{7.12A_s}{Ad}\right)^{-\alpha/(\alpha_s-\alpha)}\left[1 + \left(\frac{\alpha_s}{\alpha_s-\alpha}D - \frac{\alpha}{\alpha_s-\alpha}D_s\right)\left(-\frac{7.12A_s}{Ad}\right)^{\omega/(\alpha_s-\alpha)}\right] + B + \frac{7.12B_s}{d} \ . \tag{16}$$

The above expressions are correct to leading order in the correction to scaling terms *if these are small relative to 1.* To identify terms in these last equations with Eqs. (3) and (6), respectively, we can write them as

$$t_m = a_0 d^{-1/(\alpha_s-\alpha)}(1 + a_1 d^{-\omega/(\alpha_s-\alpha)}) \ , \tag{17}$$

and

$$C_m = \frac{A}{\alpha_s}\ln d + \alpha b(1 + b'\ln d) + b_1(1 + b_1'\ln d + b_1''\alpha\ln d)d^{-\omega/(\alpha_s-\alpha)} + b_2 d^{-1} + b_3 \ . \tag{18}$$

The constants a's and b's in Eqs. (17) and (18) involve of course the bulk and surface parameter displayed explicitly in Eqs. (15) and (16). Equation (15) is identical to leading order with Eq. (3) if one makes the scaling assumption[1,26]

$$\alpha_s - \alpha = \nu \ . \tag{19}$$

Equation (18) is also the same to leading order as Eq. (16), but contains in addition logarithmic corrections. Some of these appear because $\alpha \neq 0$ but others will remain even in the limit of $\alpha = 0$.

As an overall scaling of the data in the neighborhood of T_λ we obtain from Eqs. (11), (14), and (13) that

$$[C(t,d) - C(t,\infty)]\frac{d}{7.12} = \frac{A_s}{\alpha_s}t^{-\alpha_s}(1 + D_s t^{\omega}) + B_s \ . \tag{20}$$

This is of course identical to Eq. (12) once Eq. (19) is assumed. It is indeed from the point of view of bulk-plus-surface free energy that we suggested Eq. (12) in the previous section. One can understand more clearly now why Eq. (12), and of course Eq.

(20) cannot be applied to a region too close to T_λ: the ansatz (13) breaks down once $\xi \gtrsim d$.

In the equations above the number 7.12 Å refers to the fact that we have considered a film. For the case of a cylindrical pore this geometric factor would change, but the form of the equations would still hold. We should mention as well, that in the case of the films one might distinguish between the surface at the solid and that at the vapor. It is very likely that the two cases give different amplitudes for the surface specific heat. We cannot rule out this possibility from our data. What would be required to check on this would be a measurement on a film which is completely bound by solid surfaces. We expect that the exponent α_s is not affected by these considerations.

A. Analysis with no corrections to scaling

To use the equations from this bulk plus surface model, we start with the simplest assumption first: no corrections to scaling, $D = D_s = 0$,[28] and allowing α_s to be a free parameter. Equations (15) and (16) can then be written as

$$\ln t_m = -\frac{1}{\alpha_s - \alpha} \ln d + \frac{1}{\alpha_s - \alpha} \ln\left(-\frac{7.12 A_s}{A}\right) , \qquad (21)$$

and

$$C_m = \frac{A}{\alpha_s} \ln d \left[1 - \frac{\alpha}{\alpha_s - \alpha} \ln\left(-\frac{7.12 A_s}{A}\right) + \frac{\alpha}{2(\alpha_s - \alpha)} \ln d\right] - \frac{A}{\alpha_s} \ln\left(-\frac{7.12 A_s}{A}\right)\left[1 - \frac{\alpha}{2(\alpha_s - \alpha)} \ln\left(-\frac{7.12 A_s}{A}\right)\right] + \frac{\alpha_s - \alpha}{\alpha \alpha_s} A + B + \frac{7.12 B_s}{d} . \qquad (22)$$

We remark that the limit of $\alpha = 0$ is not easily taken in Eq. (22), but it is rather better to start with a logarithmic function at the onset. We now fit the data of the shift to Eq. (21) by treating the films and pores independently. This is of course the same as fitting the data to Eq. (1) only the results are now in terms of α_s and A_s. These are given in Table V.

Next we look at the specific-heat maximum. An inspection of Eq. (22) reveals that it is not easy to extract information from this equation. In the first place, unlike in Eq. (21), all three surface parameters appear, and secondly, the form of the equation is rather awkward. We proceeded as follows: We first of all used the values of α_s and A_s obtained from the analysis of t_m and then calculated B_s from Eq. (22). For both the pores, and the films we found that B_s is very small and could just as well be set equal to zero.

TABLE V. Results of fitting the specific heat to the bulk-plus-surface model. Values of parameters in parentheses indicate that they are held constant. All errors are standard errors except when in parentheses. (A) Analysis without correction to scaling, $D_s = 0$. α_s, A_s, B_s are free to vary. (B) Analysis with corrections to scaling, $\alpha_s = \alpha + \nu = 0.655$, $\omega = 0.5$, $D = -0.02$. A_s, B_s, D_s are free to vary.

(A)	α_s	A_s (J mol^{-1} K^{-1})	B_s (J mol^{-1} K^{-1})	Equation
Shift, films	0.508 ±0.043	−9.4 ±0.8		(21)
Shift, pores	0.563 ±0.046	−13.5 ±3.5		(21)
Maximum, films	0.53 ±(0.05)	(−9.4)	(0)	(22)
Maximum, pores	0.52 ±(0.06)	(−13.5)	(0)	(22)
Scaling function	0.450 ±0.013	−10.9 ±0.7	−4.5 ±9.6	(20)
(pores, $T < T_\lambda$)	0.452 ±0.012	−10.8 ±0.7	(0)	(20)
Scaling function	0.433 ±0.016	−6.8 ±0.6	11.3 ±9.2	(20)
(pores, $T > T_\lambda$)	0.444 ±0.016	−6.2 ±0.6	(0)	(20)

(B)	A_s (J mol^{-1} K^{-1})	D_s	B_s (J mol^{-1} K^{-1})	Equation
Shift, films	−3.1 ±(0.2)	2.9 ±(1)		(23)
Shift, pores	−3.4 ±(0.2)	42 ±(10)		(23)
Scaling function, (pores, $T < T_\lambda$)	−2.32 ±(0.09)	20.1 ±2.0	(0)	(20)
Scaling function	−1.10 ±0.04	31.3 ±4.4	−18.0 ±13	(20)
(pores, $T > T_\lambda$)	−1.0 ±0.06	27.3 ±4.0	(0)	(20)

This result will also be reinforced by our analysis with the scaling function, as we will see shortly. To get any information out of Eq. (22) we thus assumed $B_s = 0$. Further, since the terms in the curly brackets multiplying the $\ln d$ dependence are small corrections, vanishing for $\alpha = 0$, we calculated these terms by using the results from Eq. (21). Using this procedure we were able to extract α_s from the prefactor of the $\ln d$ term. These values of α_s for films and pores are listed in Table V. Here, to emphasize our procedure, we have indicated by the numbers in parentheses that the values for A_s and B_s are assumed. The values of α_s are in good agreement with those obtained in a much more direct way from Eq. (21). The errors we quote for α_s are not standard errors but reflect more closely our procedure of analysis. Lastly, we point out that to obtain α_s we used the value of $A = 6.16$ J/mol K (Ref. 24) for the specific-heat amplitude of bulk helium, Eq. (11). α_s, as obtained from C_m, is thus subject to possible systematic errors in this quantity. With all this, we can say that while the values of C_m support the results from t_m and, as we will see shortly the results from Eq. (20), they clearly do not make by themselves a very strong case for the value of α_s.

Lastly, we fit the data in the neighborhood $t \lesssim 10^{-2}$ to Eq. (20), with $D_s = 0$. We use the cutoff for small t such that the correlating length is approximately equal to the pore diameter. This in practice means $t \gtrsim 10^{-4}$. Only pore data were used in this analysis since in the case of the films very little data fell within the applicable temperature bounds. For $T < T_\lambda$, a least-squares fit yields values of α_s, A_s, and B_s; these are given in Table V. The quality of the fit is quite good, as can be seen from Fig. 4. Not only does Eq. (20) fit the data with no systematic residuals, but also the scaling with size seems quite good. In looking at Fig. 4, and Fig. 5 as well, one should keep in mind that what is being analyzed is the small difference between large numbers, this is the source of the scatter of the data. As far as the parameters obtained from the fit, we see that A_s agrees very well with the determination of A_s from t_m only. In the case of B_s, its value first of all is such that, as can be verified from Eq. (22), it would contribute negligibility to C_m. Secondly, its magnitude is zero within the standard error. This justifies in the case of the filled pores the assumption of setting $B_s = 0$ when testing Eq. (22). Indeed one can set $B_s = 0$ in the case of Eq. (20) and do a two-parameter

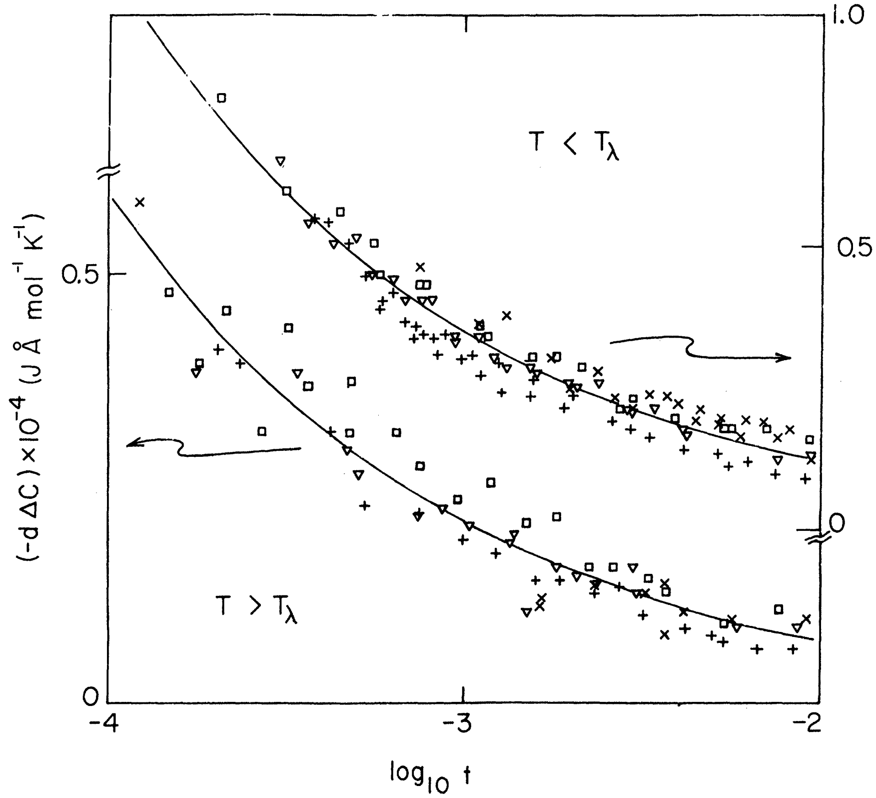

FIG. 4. Difference between the confined and bulk specific heats, ΔC, fitted to the scaling function, Eq. (20). The solid lines are results of least-squares adjustment of α_s, A_s, and B_s independently on either side of T_λ. The symbols refer to x, $d = 300$, + = 800, ▽ = 1000, □ = 2000 Å.

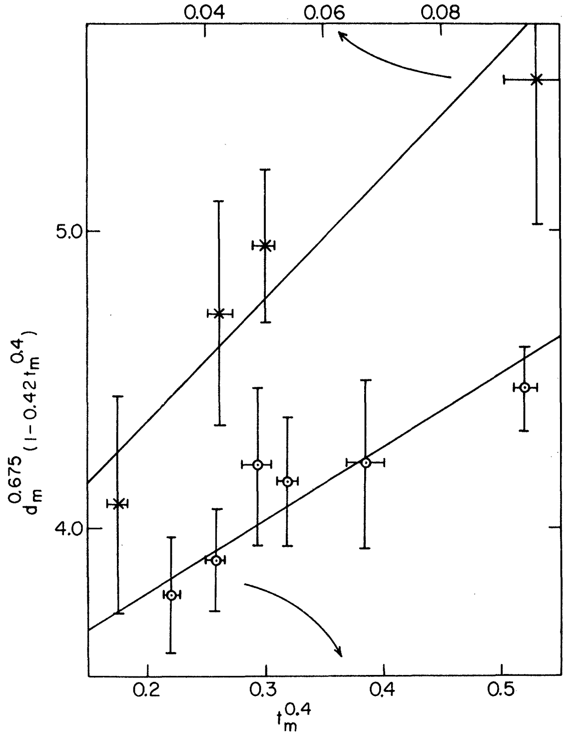

FIG. 5. Data for the shift of the specific-heat maximum plotted according to Eq. (23) to extract the leading amplitude and the correction to scaling. The ×'s refer to the filled pores and O's to the films.

fit, i.e., vary α_s and A_s only. One obtains just as good a fit as with three parameters. The result for this is also given in Table V. One can see that the values of α_s and A_s are hardly affected. The values of α_s we have obtained so far for $T < T_\lambda$, from Eqs. (21), (22), and (20), should all agree. We see that the differences are at most within two standard errors. We consider this quite good in light of the analysis. Further, we emphasize that in the case of the maximum, and shift the data are handled quite differently from the case of the scaling function. In the former, one uses absolute values of C_m and t_m, while in the latter, one uses the difference between bulk and confined specific heats at various values of t. These differences in procedure obviate possible systematic errors. The temperature range, as already pointed out, is also quite different for the films and pores.

We now fit the data for $T > T_\lambda$ to Eq. (20) with $D_s = 0$. The result of the fit is also shown in Fig. 4, and the parameters α_s, A_s, and B_s are listed in Table V. Again, as for the case of $T < T_\lambda$ we tried a fit where B_s is set equal to zero. The quality of the fit is just as good and α_s and A_s are hardly affected, see Table V. From this analysis of the data for $T > T_\lambda$ we find α_s to be in good agreement with α_s for $T < T_\lambda$, scaling among surface exponents!

$$\alpha_s = \begin{cases} 0.450 \pm 0.013, & T < T_\lambda \\ 0.433 \pm 0.016, & T > T_\lambda \ . \end{cases}$$

In both cases the results differ from the expected scaling relation between surface and bulk exponents

$$\alpha_s = \nu + \alpha = 0.655 \pm 0.004 \ .$$

Our conclusion from the above is that the specific-heat data of helium confined to films from 17.2 to 53 Å, and to pores of 300- to 2000-Å diameter are well represented by a bulk plus surface model. This does not require corrections to scaling to account for any systematic deviations from the trial functions. The model involves only three parameters, since $B_s = 0$ for $T \gtrless T_\lambda$ and the exponents α_s are equal. The cost of this simplicity and symmetry is that the characteristic exponent α_s *does not agree with the scaling prediction.* This conclusion is no different from that reached in Sec. III, but is much stronger because of the more explicit functions used.

B. Analysis with corrections to scaling

Next we analyze the data to see if the scaling prediction for α_s can be retained by absorbing the remaining temperature dependence in the correction terms. For the shift, Eq. (15), we already know the answer since it is of the same form as Eq. (3) which we have used already. However, we can do a better job now which does not involve the assumption that the D_s term is small. We emphasized that to obtain Eq. (15) this was a necessary assumption. To avoid this we proceed directly from the condition of the maximum, i.e., $d^3F/dT^3 = 0$, and we have

$$t_m^\nu d\left[1-\frac{\omega-\alpha}{\alpha}Dt_m^\omega\right] = \left[-\frac{7.12A_s}{A}\right]\left[1-\frac{\omega-\alpha_s}{\alpha_s}D_s t_m^\omega\right] \ . \tag{23}$$

By plotting the left-hand side vs t_m^ω we obtain A_s and D_s. These values are listed in Table V for the case of $\omega = 0.5$. Indeed, as we remarked in the case of Eq. (3), the data cannot discriminate very sensitively the value of ω. The case of $\omega = 0.4$ is shown as an example in Fig. 5. If one performs the analysis with Eq. (15) rather than Eq. (23) the results for A_s are unchanged within the errors, but the values of D_s are substantially larger, i.e., a factor of 6 for the films and a factor of 2 for the pores. This is not surprising in light of the fact that Eq. (15) is only the leading order expansion of Eq. (23), and really only valid for much smaller values of D_s than in our case.

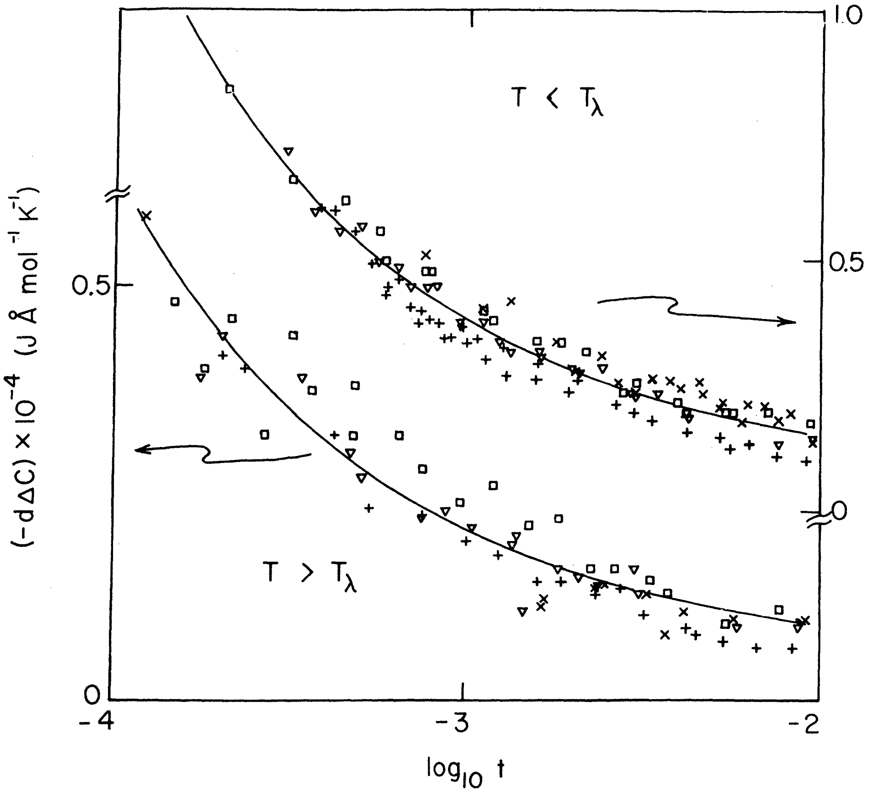

FIG. 6. Difference between the confined and bulk specific heats, ΔC, fitted to the scaling function, Eq. (20). The solid lines are results of least-squares adjustment of A_s, B_s, D_s independently on either side of T_λ. The symbols have the same meaning as in Fig. 4.

In the case of the specific-heat maximum we are again confronted with a rather intractable equation, even more so than when we considered the case with $D_s = D = 0$. We chose not to use Eq. (16) to obtain values of A_s, B_s, or D_s, but rather only to check if the results from Eqs. (23) and (20) are consistent with Eq. (16). This indeed turned out to be the case.

Lastly, we fit the pore data near T_λ with Eq. (20). We did this by varying A_s, D_s, and B_s as independent parameters above and below T_λ. The fits achieved can be seen from Fig. 6 to be just as good as in the case of $D_s = 0$ and α_s a free parameter. Thus, on the basis of the goodness of these fits, no preference can be made between these two possibilities. However, as we have observed all along, the correction-to-scaling terms needed to retain the relationship between surface and bulk exponents, Eq. (19), are large. The amplitude is 20 to 30 times the leading amplitude, or a factor of $\sim 10^3$ larger than the correction-to-scaling amplitude for the bulk specific heat. In the case of the films, where only the value of D_s from the shift has been obtained, we find it only ~ 3 times the leading term, or $\sim 10^2$ times the analogous bulk term.

VI. COMMENTS

A. Other measurements of specific heat

There have been many measurements of specific heat of helium films, and one might wonder whether these data are compatible with the results discussed in this paper. For almost all the data, which are in the "right" thickness regime, we have already mentioned in the Introduction their common, dominant qualitative feature of a rounded maximum below T_λ. By the "right" thickness regime we mean films thicker than ~ 4 layers where the physics of finite-size effects are more clearly manifest. Clearly for thickness of the order of a monolayer the dominant effects are quite different. This perhaps can be best epitomized by the very extensive data of near monolayer films on Grafoil.[29] Our focus with thick films is obviously quite different.

The exception to the rounded specific heats of films is the data of Bretz for multilayers on Grafoil.[30] Some explanations have been proposed for this behavior,[3,31] but perhaps the simplest might be inhomogeneity of film thickness due to capillary condensation. This might occur in regions where the graphite crystals are very close or touching. Among the other data only those of Frederikse[5] agree with the determination of the shift in the maximum with size.[9] The value of the specific-heat maximum is not in agreement, but this can be easily explained by a slight error in the vapor contribution. This goes back to our remark that the position of the maximum is not affected very much by the vapor correction (hence the agreement), while the maximum itself is very sensitive.

The data for films in Vycor glass were historically the first for which agreement with the scaling prediction for the shift exponent was suggested.[32] It seems clear now that these data must suffer from capillary condensation in the Vycor pores. The film thickness used exceed the limit for capillary instability. This explanation is also consistent with the observation of a difference between the onset of superflow and the specific-heat maximum. This would be due to the difference in the confining dimension of the film and the capillary-condensed filled pores. In addition to these considerations, it seems clear that confinement of helium in Vycor, whether films or filled pores, is a rather unique situation. It has been observed for instance[4] that the superfluid fraction even for very dilute films (~0.06 of a full layer above an inert layer) is three dimensional in character. In addition, in the case of the specific heat of filled Vycor, it has been emphasized that there is no way to reconcile it with predictions of finite-size effects.[10]

Lastly, as a general statement for all the data on the specific heat of thick films we point out that none are for films of constant thickness. The thickness varies as the temperature increases and evaporation takes place. Even a proper correction for this leaves the data as the specific heat of a helium film along a thermodynamic path unique to a particular calorimeter. This has little effect if one just compares say the maximum, but it has a marked effect on the shape of the specific heat. Thus there exist no data on thick films on various substrates which can be said to agree over a substantial temperature range.

B. Measurement of the onset of superfluid flow

Measurements of flow onset and superfluid density are another, and perhaps more relevant, way of determining the transition of confined helium. If one accepts the scaling prediction, the behavior of this onset with size should be governed by the same exponent, $1/\nu$, as the shift in the specific-heat maximum. If one allows for a failure of scaling, then this need not be so, and the two shift exponents might differ. As a matter of experimental procedure we point out that the determination of the confining dimension is subject to the same caveat of homogeneity as in the case of the specific heat. Further in the case of inhomogeneous confinement the flow measurements yield a transition which is biased to the smallest confining dimension as opposed to the case of the specific heat which is biased toward the largest dimension.

We will not review the flow measurements here, but point out that recent data by Brooks, Sabo, Schubert, and Zimmermann[33] for the vanishing of ρ_s in Nuclepore filters favor a shift exponent of $1/0.53 \pm 0.08$. This differs from the scaling prediction of $1/0.675$, and is very much in agreement with our determination from the specific heat. Further, Brooks *et al.* point out that their result is consistent with other filled channel experiments which also favor an exponent greater than $1/\nu$. Thus, a more global view of these experiments tends to support our observation from the specific heat of a failure of leading order scaling predictions.

In addition to the shift exponent there have been recent measurement by Agnolet, Gasparini, and Reppy[34] of the superfluid density of helium confined in a region ~4000 Å between sheets of Mylar. These data suggest that the deviations from bulk behavior in a region not too close to the transition, $t \gtrsim 3 \times 10^{-5}$, can be analyzed very much in the spirit of bulk-plus-surface contributions. The resulting surface exponent seems to disagree with the scaling prediction in the same way as for α_s.

C. Thermal expansion

The thermal expansion, which in bulk helium has the same singularity as the specific heat, should manifest similar finite-size effects. Measurements for helium confined to packed powders, and Vycor glass, have been reported by Wiechert and Wupperfeld.[35] Their data are consistent with Eq. (1) and $\Lambda = 1/\nu$. However, as we already discussed, packed powders and Vycor do not give the necessary well-defined confinement to test Eq. (1). Hence, we would take these data as giving only a qualitative support to finite-size scaling.

D. Crossover in dimensionality

We have not used in our discussion of finite-size effects the concept of crossover into a lower dimensionality. It does not seem to matter, for the specific heat, that the films, once the correlation length is of the order of thickness, are really two dimensional (2D). For the same reason the full pores would cross over into a one dimensional regime. In the case of the films, the 2D behavior, as far as the onset, is described well by the Kosterlitz-Thouless theory.[36] According to this theory one expects a small maximum in the specific heat at a temperature *above* the 2D transition. At the transition the specific heat is perfectly regular.[37,38] What seems to be happening for the films we have analyzed is that the maximum resulting from finite-size effects dominates the 2D behavior, thus the data are more aptly analyzed as we have done. Of course, a more complete description would involve functions which display the full range of behavior, from finite size 3D to 2D since no real dichotomy in these points of view exists.[39]

In the case of the filled pores, when the data are analyzed according to the scaling function, Eq. (20), the crossover into another dimensionality is irrelevant as far as the value of the exponent α_s. The only way in which the geometry enters is via the amplitudes A_s, B_s. Another way of saying this is that if we think of deviations from bulk behavior as being a surface effect, then it matters little what the geometry is. At least as long as we are in a region where the correlation length is smaller than the smallest dimension. Of course if one wants to scale the data with size, then the geometry does enter. The confinement to say a 1000-Å film is obviously not equivalent to a 1000-Å-diameter pore.

E. Measurements on other systems

There are no measurements of specific heat on any other systems which have addressed themselves to finite-size effects. In the case of nickel however, there are measurements by Lutz, Scoboria, Crow, and Mihalisin[40] of the resistivity near the ordering transition for films in the range of 250 to 24 000 Å. The derivative of the resistivty with temperature, $d\rho/dT$ is expected to be analogous to the specific heat. An analysis of the shift of the maximum in $d\rho/dT$ with size yields an exponent $1/\Lambda = 0.99 \pm 0.1$ in disagreement with the scaling prediction $1/\Lambda = \nu \cong 0.70$. It was also found that the data near the transition did not scale satisfactorily.

In another universality class (Ising), there have been measurements of the coexistence of films of methanol cyclohexane by Jacobs, Mockler, and O'Sullivan[41] which seemed to give a logarithmic shift in T_c. This result has been called into question by Meadows, Sheibner, Mockler, and O'Sullivan[42] after their measurements of 2,6-lutidine and water. With this system they find good agreement with scaling predictions both as far as the shift exponents, and the scaling of the data with thickness. These data, however, also show a marked effect from the boundary conditions of the fluid at the walls. A silvered mirror results on an enhancement of the 3D transition temperature, while a dielectric mirror showed a depression. This enhancement and depression they find are not governed by the correlation length exponent. These effects are possibly due to the van der Waals field of the walls which couples directly to the order parameter. This would have a marked effect on the transition. This difficulty is not present in the case of the helium experiments.

F. Some theoretical results

There have been many theoretical calculations of thermodynamic functions to look at size effects near a critical point. These have involved various methods, series expansions, renormalization group, Monte Carlo computer experiments, and rigorous calculations. Overall the results tend to support the scaling conjectures, and there is no case where corrections to scaling have been needed to achieve agreement. Nevertheless, there is no real ground to find a serious discrepancy with the results of our analysis. In the first place most calculations have been done on systems of different universality class from helium. Secondly, many calculations, which involve either fully finite lattices in two or three dimensions or semi-infinite lattices with a finite number of layers, are done for cases where the smallest dimensions are in a range which, judging from our results, is outside the asymptotic region where, say, Eq. (1) would hold. Thirdly, many theoretical calculations lack the precision to test the scaling prediction in a crucial manner.

We will not attempt a review of the theoretical work, but will discuss some which are most relevant to our own results. In the case of the infinite 2D Ising model with a surface there are exact calculations by McCoy and Wu[43] and Ferdinand and Fisher[44] of the surface specific heat. They find that it diverges as t^{-1} in precise agreement with the scaling prediction of $\alpha_s = \alpha + \nu$, $\alpha = 0$, $\nu = 1$. In the case of the semi-infinite 2D model, strips $\infty \times L$, Au-Yang and Fisher[45] have found agreement with the scaling prediction of $\Lambda = 1/\nu$ for strips in the range of $2 < L < 64$. They also find that a bulk-plus-surface decomposition for the specific heat is quite reasonable for $\xi/L \lesssim 0.5$ for $T < T_c$, and $\xi/L \gtrsim 0.1$ for $T > T_c$. For $T > T_c$, this is not significantly different in range to what we have used in our own analysis if we take L approximately equal to the diameter of pores. Further they find that the residual of a surface-plus-bulk decomposition decays exponentially in L/ξ as one moves away from T_c.

In the particular case of the shift exponent Bray and Moore[46] have obtained an expression for Λ to order $\epsilon = 4 - D$. This result for Λ is directly relevant to the experiment with helium. However, the precision of the calculation, to order ϵ, is not high enough to test the scaling prediction at the level of our experiment. To see this, we note that the order ϵ calculation for the bulk correlation length exponent is less than the true value of ν by ~ 0.08. If one assigns this very likely error to the order ϵ calculation of Λ, then no real discrepancy exists. This theoretical result agrees both with scaling and our own experimental results.

In the case of the 3D Ising model there are calculations by Allen[47] and Allen and Fisher[1] of the susceptibility of films $\infty \times \infty \times L$. For a free surface boundary condition the results for the shift in T_c are consistent with $\Lambda \cong 1.56$. However for periodic conditions one finds $\Lambda \cong 2.0$. The results for the free surface do not seem to exclude, however, a somewhat lower value of Λ, possibly ~ 1.3. The range of films considered $2 \leq L \leq 7$ covers a region where from helium experiments substantial deviations from Eq. (1) occur. On this same point, the exact calculations of the magnetization of finite cubes by Binder[48] and Monte Carlo calculations by Binder and Hohenberg[26] and cubes $55 \times 55 \times L$ with $L = 2, 3, 5, 10, 20$ show substantial deviations from Eq. (1), if L is too small.

Capehart and Fisher[49] have calculated the susceptibility scaling function for Ising films of $\infty \times \infty \times L$ with L up to 14 for periodic boundary conditions and $L = 10$ for free surface. Among their results they have obtained an effective susceptibility exponent as function of ξ/L. One finds from Fig. 9 in their paper, that by the time $\xi \cong L$ the effective susceptibility exponents is $\sim$80% of its crossover to the 2D value for a free surface and $\sim$67% for periodic boundary conditions. One conclusion which one might infer from this is that the condition ξ less than or approximately equal to the pore diameter we imposed in fitting our data to the bulk-plus-surface model is not too unreasonable. Indeed the success of the model might argue for the boundary condition of a helium film being closer to periodic rather than free surface. All this, however, should be taken with a grain of salt since one is indeed comparing not only different universality classes, but also different thermodynamic functions.

Landau[50] has done Monte Carlo studies of the finite Ising square lattice $L \times L$ with $L \leq 64$. In the case of the shift of the transition temperature as determined from the specific-heat maximum the results are consistent with scaling for both periodic boundary conditions and free edges. In the case of periodic boundary conditions good agreement is also found with the calculation of Ferdinand and Fisher.[51] If, however, one determines the shift in T_c from the maximum in the susceptibility, systematic deviations from scaling seem to manifest for both types of boundary conditions. Landau also finds that the specific heat can be analyzed as a bulk plus a surface contribution, and this scales as tL^{θ}, with $\theta = 1/\nu$. The scaling function is a simple power with exponent $\alpha_s = \alpha + \nu$. This scaling plot, Fig. 19, is very reminiscent of Fig. 3 of Chen and Gasparini,[11] although in the latter's case, the scaling exponent was not $1/\nu$. A comparison of these two figures shows that the range in which the theoretical and experimental plots yield a power law is quite comparable $tL^{\theta} \gtrsim 1$ for the Monte Carlo data and $tL^{\theta} \gtrsim 3$ for the experiment.

VII. SUMMARY AND CONCLUSIONS

From the analysis of the specific heat of confined helium, the simplest picture which emerges is one in which the deviations from bulk behavior are ascribed to a surface term in the free energy. This gives consistent results for all aspects of the measured specific heat, and is especially simple when it comes to the scaling function near T_{λ}. A simple power law scales all the data above and below T_{λ}. All aspects of the data can be described by only three parameters: two amplitudes and one exponent, α_s. This exponent is found to be the same above and below T_{λ}, but in disagreement with the surface scaling prediction of $\alpha_s = \alpha + \nu$. One might conclude from this that the presence of surfaces manifests a new critical length, with exponent ν_s.

To retain the scaling prediction, the bulk-plus-surface model gives a natural way to include correction-to-scaling terms. The equations for the maximum and the shift are very much in keeping with those suggested by Fisher. An analysis which includes these terms shows them to be very large, typically 20 to 30 times the leading amplitudes, and very much larger, by three orders of magnitude, than what is encountered in the case of bulk helium.

We find that the analysis in terms of the surface specific heat, which we believe is the first for an experimental system, to be quite in keeping with some theoretical work, especially as far as the range in temperature where the model should apply. We also find that our results, although not in agreement with scaling predictions, are not, nevertheless in serious disagreement with theoretical calculations.

ACKNOWLEDGMENTS

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APPENDIX: EFFECT OF THE PRESSURE GRADIENT ON THE SPECIFIC HEAT OF THE FILMS

We want to consider in this Appendix the effect of the pressure gradient due to the substrate's attraction of the helium film. One might think of this effect as a possible source for the disagreement with leading order scaling predictions we have discussed. That this cannot be the case, can be quickly established by recalling that our results of deviations from scaling are manifest both with the films and the filled pores. In the latter case the effect of the substrate potential is negligible. Even in the case of the films, where this potential is substantial for a good percentage of the sample, we will see that a reasonable model does not yield an explanation of our data. It is constructive, nevertheless, to go through this calculation to get a feeling of the order of the effect.

The model we will use is as follows: We consider a film of helium bound to a substrate via the van der Waals force. This produces a local pressure in the film which varies with position and is essentially zero at the liquid vapor boundary. The specific heat of atoms in this film can be thought of as being a function of position (pressure). At each pressure one has a different $T_\lambda(P)$, thus for fixed temperature the helium at various positions in the film is at different values of the variable $[T - T_\lambda(P)]$. By adding up contributions from different positions of the film one can construct the total heat capacity. This model is certainly not correct because it treats the film as an uncorrelated collection of independent "slabs" of helium. Nevertheless we might trust the results as a first-order estimate.

The relationship between the pressure, the molar volume, v, and the van der Waals potential energy $U(z)$ is[52]

$$-v\,dP = dU(z) \ . \tag{A1}$$

We integrate this equation by evaluating $\int_0^P v(P)\,dP$ numerically and parametrizing the result. We have

$$-27.1P + 0.1P^2 = U(d) - U(z) \ , \tag{A2}$$

where d is the thickness of the film—we now count the first solid layer in this thickness—and z is the distance from the substrate. For $U(z)$ we have

$$U(z) = \frac{\gamma}{z^3} = -\frac{2.4\times10^{-37}\ \mathrm{erg\,cm^3}}{z} \ , \tag{A3}$$

where we have used the value of γ as determined in Ref. 12. Equation (A2) can be solved for the $P(z)$ and then one can construct the total heat capacity C as

$$C = \sum_{i=1}^{n} N_i C_{P_i}(t_i, P_i) \ . \tag{A4}$$

For summation purposes, one has divided the film in n slabs each at a different pressure and with number of moles N_i. To implement Eq. (A4) we have used the expression for the specific heat

$$C_P = -A_0 \ln|t| + B_0 + D_0 t \ln|t| + E_0 t \tag{A5}$$

with the pressure-dependent amplitudes as given by Ahlers.[53] An example of our calculation of C for four films is shown in Fig. 7. The first striking feature of this graph is the "wavy" nature of the calculated points. This is a trivial result which depends on the division of the film into "slabs" with their own local $T_\lambda(P)$. The many peaks depend on how close to these T_λ's one calculates their specific-heat contributions. Clearly this is an unrealistic result which we could have avoided by introducing a

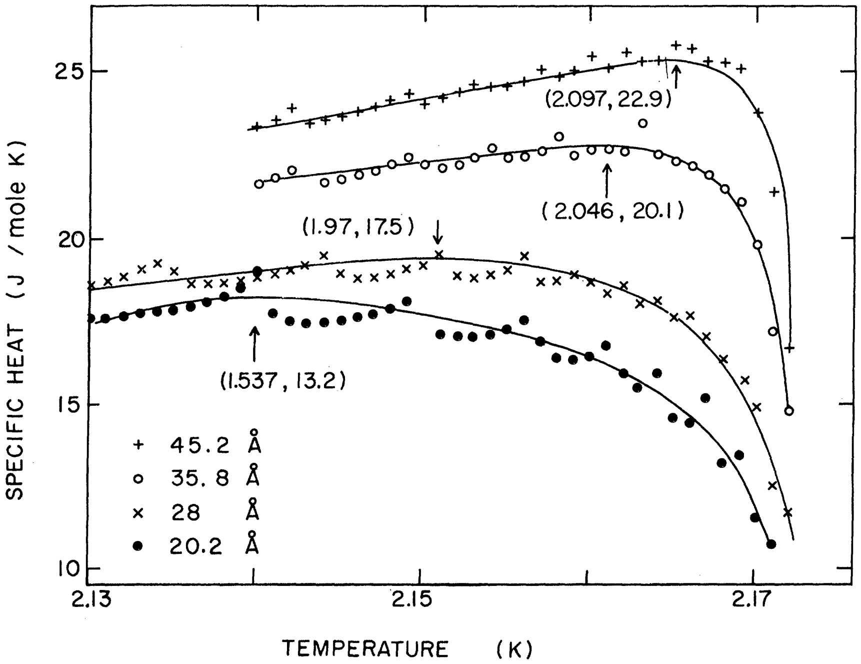

FIG. 7. Specific heat of helium as calculated from bulk properties. The numbers near the maxima indicate the experimental values for the temperature and magnitude of the specific-heat maximum. The thickness indicated for each case refers to the total thickness above the substrate. The solid lines are drawn to guide the eye.

"smoothing function" in Eq. (A4). The solid lines through the points—drawn by eye do just as well. The main result of Fig. 7 is that the maxima are very much closer to T_λ than in the case of the experimental measurements. The position of the expeirmental maximum is indicated for comparison as the first number near each curve. The calculated specific heat at the maximum is of the same order as the experimental result—the second number near each curve.

One might now suggest that the total shift in the maximum is a combination of a "trivial" effect due to the pressure and one due to the correlation length. We have tried this approach and "corrected" the total temperature shift by subtracting the shift due to the pressure only. This amounts to $\lesssim 10\%$ correction to t_m. We then reanalyzed the "corrected t_m" to extract the shift exponent. We found $1/\Lambda \cong 0.55$, essentially unchanged from the "uncorrected t_m" analysis which gave $1/\Lambda \cong 0.53$ (see Table III).

We conclude that the pressure effect, although an interesting exercise, does not explain within our model the leading order disagreement with scaling.

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[28] In fact, taking $D = 0$ has little effect on the analysis and is simply used for simplicity. The crucial step is setting $D_s = 0$. In fitting the data to the scaling function, Eq. (20), the assumption $D = 0$ is not needed at all.

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