Precision Specific-Heat Studies of Thin Superfluid Films

Lindsay M. Steele, Charles J. Yeager, and Daniele Finotello
Department of Physics, Kent State University, Kent, Ohio 44242
(Received 5 February 1993)

We report precision specific-heat measurements for two-dimensional helium films in Anopore membranes and in Millipore filter paper. Above the transition temperature and for films less than a superfluid layer thick, we find a distinct specific-heat peak which can be understood in terms of the Kosterlitz-Thouless vortex unbinding mechanism. Although our results are well described by the planar theory, transition broadening becomes evident for thicker films.

PACS numbers: 67.40.Kh, 67.40.Hf, 67.40.Rp

The 2D superfluid transition is well known within the framework of the Kosterlitz-Thouless (KT) theory [1]. This theory predicts that the specific heat is an increasing function of temperature which is regular at the transition T_c (an unobservable essential singularity) followed by a round peak, with a maximum at $T_m > T_c$, due to the entropy increase as vortices unbind. To date, no unambiguous experimental observation of this KT prediction exists [2]. Computer simulations have observed this nonuniversal peak [3] and estimated the shape, width, and position, but the detailed features are model dependent.

In this Letter, we present the first specific-heat measurements for films in the nearly cylindrical pores of Anopore membranes [4] and in the 3D connected pores of Millipore fibrous filter paper [5]. For films in both substrates, we find a specific-heat peak at temperatures above the superfluid transition and study the peak dependence on thickness and temperature. We interpret this peak in terms of the KT vortex unbinding mechanism. Although our results conform to expectations from the KT theory, they also indicate that transition broadening is present and becomes more important for thicker films.

Anopore membranes are made from a high purity alumina matrix using an electrochemical anodizing process [6]. The 60 μm thick Anopore possess 0.2 μm diam pores which are much larger than the film thickness [7]. They were chosen over the better known Nuclepore [8] because their larger surface area, uniform pore size distribution, and smoother pore wall [9] make them better candidates to probe the helium films' planar properties. We made scanning electron microscope (SEM) photographs of the 3D connected pores of our Millipore filters which are type VM with nominally 0.05 μm pore diameter. The SEM revealed a typical pore size closer to 0.5 μm, consistent with other measurements [10]. Though Millipore is highly interconnected, superfluid-density studies [10] did not observe a power-law critical region near the superfluid transition. Helium films in these two substrates can be treated as planar.

ac calorimetry [11] was used on two Anopore cells of 1.76 and 4.37 m^2 and a Millipore cell of 3.66 m^2 surface area. The membranes were tightly packed above one another inside a thin (0.051 mm) brass cuplike enclosure. The Anopore cells used membranes from different batches. All data taken were reproducible under heating and cooling, at different heating powers and frequencies, increasing and decreasing the film thickness, and after several annealings of the same film at high temperatures. Both Anopore cells also produce the same results.

Specific-heat results for films in Anopore and Millipore, less than 1 superfluid layer thick, are shown in Figs. 1 and 2. The films' specific heat data have been corrected for the empty cell contribution. As thickness increases, a round peak is seen to grow and shift to higher temperatures. Surprisingly, Fig. 3 shows that with further increase in thickness, the peak contribution to the total heat capacity is masked by a fast increasing regular background. As a result of a slightly lower specific heat, the peak can be followed in Millipore up to thicker films than in Anopore. The peak is not seen in thinner films [12] as it is too small to resolve; this is confirmed by extrapolating the peak size growth as a function of thickness to thin films. Also, as seen in Fig. 3, thicker films in Anopore develop a low temperature bump which is centered at a temperature that decreases with coverage. This bump signals a change in the temperature dependence of the

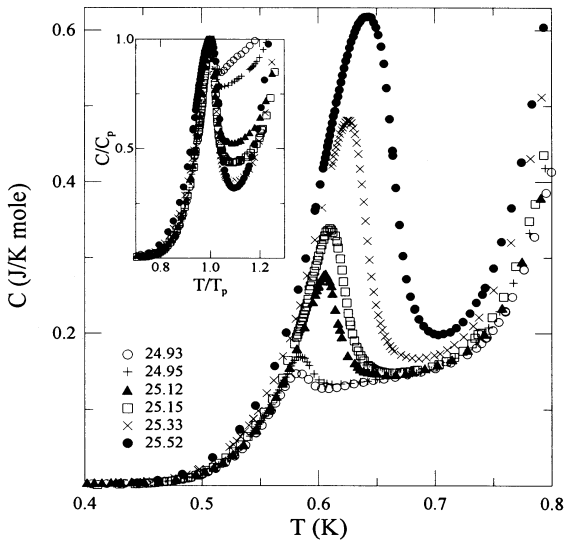

FIG. 1. Specific heat vs temperature for superfluid films in Anopore. Coverage (thickness) is in μmole/m^2. Inset: films normalized by the peak temperature and magnitude at maximum to emphasize the universal behavior.

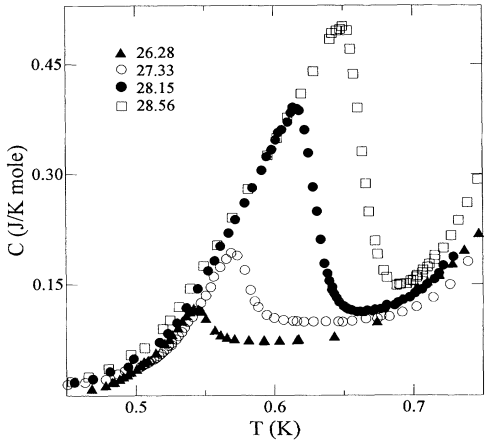

FIG. 2. Specific heat as a function of temperature for superfluid films in Millipore. Coverage is in μmole/m^2.

heat capacity. It settles at 0.38 K for films thicker than 50 μmole/m^2, where a heat capacity thickness independent limit is reached [13,14].

Because of the free surface and the underlying adsorbing substrate, the excitation spectrum for films is richer than for bulk. For thicker films, the excitation spectrum may change and new degrees of freedom become available [14,15]. This changing spectrum could be responsible for the fast growing regular background and the eventual appearance of the low temperature bump.

We have interpreted the observed peak as evidence for the KT vortex unbinding maximum. We have evaluated other mechanisms but each lacks some qualitative aspect of our results. Melting was eliminated because the peak does not grow large enough and the temperature dependence before the peak is not dominated by T^2. The peak position coverage dependence is too strong to be liquid-gas coexistence. Capillary condensation was ruled out as the peak becomes small compared to the growing background. While a round peak can indicate the finite size effects for thick films, our films are less than 1 superfluid layer thick and thus too thin to be in that regime.

More support for an interpretation that the peaks are unique to the ^{4}He superfluidity comes from probing them with ^{3}He. With increasing concentration, the peak shifts to lower temperature (as expected upon the addition of normal impurities [16]) and narrows and decreases in size [17]. No peak was found for pure ^{3}He films that were studied over a wide thickness range, 10 to 60 μmole/m^2. The complete mixtures work will be presented elsewhere.

While no previous studies have characterized superfluidity in Anopore, it is a universal feature that the superfluid transition temperature increases with film thickness. Accordingly, the peak maximum occurring above the transition temperature must shift upward in temperature. Figure 4 shows that the Anopore peak shifts linearly with thickness. From this we estimate the critical coverage for superfluid onset in Anopore at 20

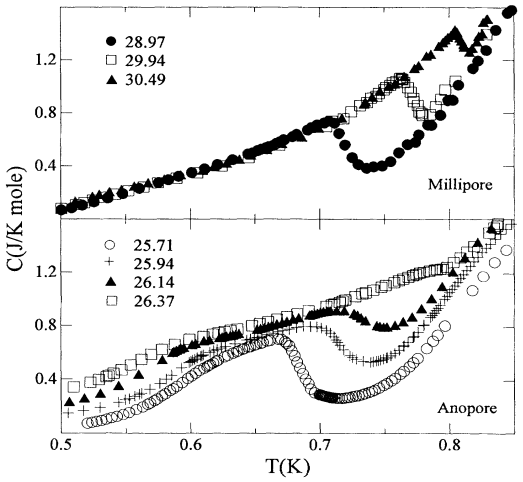

FIG. 3. Evolution of the vortex peak with thickness. Note its smaller contribution and the fast growing regular background, and the overlap of the Millipore data up to the peak. The Anopore films, also overlapping, were shifted upward 0.1 (+), 0.15 (▲), and 0.25 (□) J/mole K.

μmole/m^2, compared to 24.6 μmole/m^2 in Millipore [10]. The Anopore result suggests an inherently weak van der Waals attraction which should render studies with hydrogen preplated Anopore interesting [18]. Third sound velocity studies to find the transition temperature and its coverage dependence are needed.

The Millipore peak temperature position vs coverage is

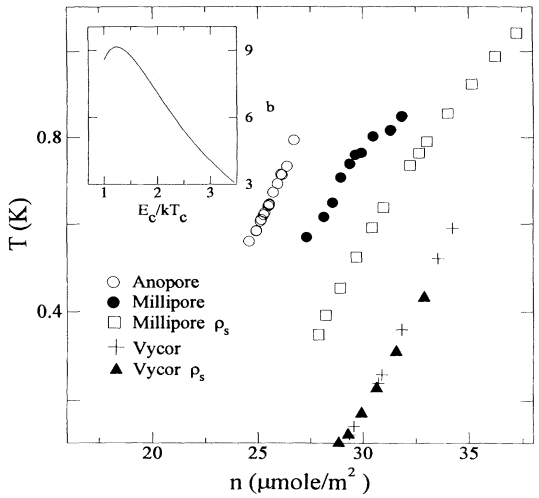

FIG. 4. Specific-heat peak temperature vs coverage. The superfluid transition temperature as obtained from the ρ_s measurements in Millipore [10] is also shown. Also included are the temperature position of the sharp specific-heat signature (+) [20] and the transition temperature from the superfluid-density studies (▲) [21] in Vycor to emphasize their coincidence. Inset: the nonuniversal constant b as a function of E_C/k_BT_c given by Eq. (2).

shown in Fig. 4. Also included is the coverage dependence of the transition temperature obtained from superfluid-density measurements [10]. The peak temperature is clearly above the transition, with the temperature separation decreasing with coverage. We take this to indicate that the manifestation of the 2D behavior is relegated progressively closer to the transition temperature as a film thickens [19]. Since the comparison with Ref. [10] involves different batches and depends on the respective surface areas, the peak is probably closer to the transition temperature than seen in Fig. 4. A simultaneous specific-heat/superfluid-density study would resolve this.

Studies of the specific heat of helium films in Anopore and Millipore reveal a peak at a temperature above the superfluid transition, while the specific heat is regular at the transition. In contrast, in the smaller pores of Vycor or Xerogel glasses, the specific heat exhibits a small but sharp signature [20] at a temperature coinciding with the superfluid transition as determined by superfluid-density studies [21]. In addition to the sharp signature at the transition, a broad anomaly that was centered at higher temperature was found [20,22]. Although a critical exponent was not determined, the sharp signature was viewed as supporting evidence for the suggestion that the superfluid transition in porous glasses is a transition with genuine critical behavior [23]. The high temperature Vycor bump, 5 times broader than our peaks, is generally attributed to finite size rounding of the λ transition [20]. The Vycor results shown in Fig. 4 emphasize the different behavior in porous glass from that found here. Helium films in Anopore and Millipore are in a different universality class than films in Vycor glass.

Berker and Nelson and Solla and Riedel [3] predicted that the low temperature specific heat rises exponentially, goes smoothly through T_c, and reaches a maximum 30%–40% above the transition. Our peaks are well described by an exponential rise in inverse temperature up to the maximum with no other signature prior to it. Alternatively, to fit the peak region, from the KT theory for planar films [1,2,24], we write the free energy as

$$F_+(T) = -A(\xi_{2D})^{-2} + F_0(T), \quad F_-(T) = F_0(T), \qquad (1)$$

where $+,-$ denote $T > T_c$, $T < T_c$; $F_0(T)$ is a regular function, ξ_{2D} is the two-dimensional correlation length given by $\xi_{2D} = \xi_0 \exp(2\pi t^{-1/2}/b)$, $t = T/T_c - 1$, and b is a nonuniversal constant which for thin films such as ours is related to the vortex core energy [25] and is given by

$$b = 8\pi \exp(-E_C/2k_BT_c)[(1/\pi) - 2(1 - E_C/k_BT_c) \times \exp(-E_C/k_BT_c)]^{1/2}, \qquad (2)$$

but for films thicker than 1 superfluid layer, b must be related to the 3D correlation length [19,26]. The specific heat is obtained by differentiating Eq. (1) twice with respect to temperature:

$$C_- = -TF_0''(T), \qquad (3a)$$

$$C_+ = TA[2\pi t^{-5/2}/b(T_c)^2][(2\pi t^{-1/2}/b) - 3/2] \times \exp(-4\pi t^{-1/2}/b) - TF_0''(T). \qquad (3b)$$

C_+ and C_- were simultaneously fitted using two different choices for the analytic (regular) part. The results of these fits are described below and shown in Fig. 5.

The same $AT + BT^2$ was subtracted from all data to remove from the heat capacity a coverage independent contribution. These terms, obtained using data below and away from the peak region, can be attributed to glasslike behavior plus 2D phonons from the underlying nonsuperfluid layer. In the first method [panels (a) in Fig. 5], since $C_+(T_c) = C_-(T_c) = -T_cF_0''(T_c)$, the regular term was fitted up to T_c to an exponential in inverse temperature. This regular part was later fixed and assumed that near T_c, $F_0''(T) = F_0''(T_c)$ [2,25], using an iterative process. Our second method treats the background specific heat in a model independent fashion. In panels (b) of Fig. 5, the specific heat corresponding to the thickest film that did not show a peak (nonsuperfluid over the peak region) was subtracted from the films exhibiting a peak. The residual specific heat was fitted to the predicted planar vortex contribution. Reasonable fits were achieved with both methods. Because the best fits are obtained for thinner films, we suspect that thick films show the increasing importance of excitations not treated by the KT theory.

Agreement is found with the position and magnitude at the maximum and the temperature width; however, the expected vortex contribution to the specific heat given by Eq. (3) increases sharply at T_c (break in the fits). There is a more gentle rise in our data, which is not unexpected. Fits to the Millipore superfluid-density data required the

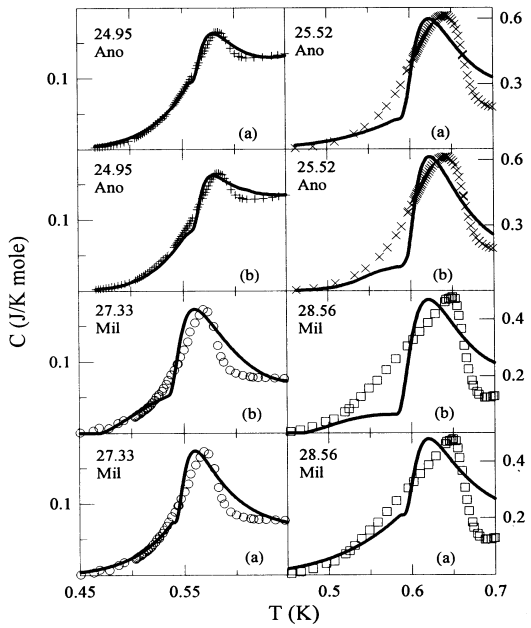

FIG. 5. Fits to Eq. (3), using two choices for the regular part, to films in Anopore and Millipore, after subtraction of $AT + BT^2$. Solid lines are fits to the data as described in text. Slight breaks in the fits indicate the transition temperature.

generalization of the KT theory by considering the effect of a cylindrical substrate on vortex interactions [10,27]. A similar extension was needed to understand the behavior of films in packed powders [28]. Also, as seen in Mylar, additional broadening of the transition may be caused by macroscopic inhomogeneities in the substrate potential [29]. If transition broadening were included, it would likely slow down the specific-heat rise towards the maximum and locate T_c at lower temperature than we find with the fits. In our fits, the peak maximum is at most 10% above T_c.

In the simulation by Tobochnik and Chester [3], they find that vortex pairs unbind at T_c. There, large clusters of vortices appear and unbind faster as the temperature is raised. The clusters are responsible for a sharp specific-heat peak which is closer to T_c than in other theories. Although our peak position conforms to their prediction, it is not sharp enough to be attributed to clusters.

The best fits are found for $b \sim 8.5$, with b showing a decreasing trend with thickness. This is expected from Eq. (2) and shown in the inset of Fig. 4. From this value of b we obtain $E_C/k_B T_c = 1.5$, which is comparable but slightly smaller than values obtained for films in other substrates [15,28]. Using the values of b and T_c from our fits, at the peak maximum $t^{-1/2} = 3.16$. This leads to $\xi_{2D} \sim 10\xi_0$, which is not much larger than the film thickness. Noting that for $t^{-1/2} < 4$ thermal conductivity studies for films over a superfluid layer thick on Mylar showed systematic deviations from the KT behavior [19], we do not expect our fits to be valid much beyond the peak.

A final feature of the data evident from Fig. 2 and the inset of Fig. 1 is its collapse onto a "universal" curve below the specific-heat maximum. This is surprising since b is a nonuniversal constant. One could argue that such collapse is a consequence of the narrow thickness regime over which the peaks are seen. This ranges from 0.3 to 0.5 and 0.2 to 0.6 superfluid layers for Anopore and Millipore, respectively [30]. Yet, the data merge in a single curve so effortlessly that although we lack an explanation it might not be fortuitous.

In summary, we reported the first specific-heat studies for 2D superfluid films in Anopore membranes and Millipore filters. The specific heat is regular at the superfluid transition temperature followed by a round peak which we interpreted in terms of the vortex unbinding mechanism. The data were reasonably described by the KT theory, but transition broadening becomes evident for thicker films and needs to be included. We mentioned the effects of adding ^{3}He to a ^{4}He film, and indicated that no peak is seen for ^{3}He films in Anopore. We compared our results with those in porous glasses and suggested alternative studies on these and in other substrates like Mylar that would resolve several outstanding questions.

We benefited from discussions with Phil Adams, Moses Chan, Milton Cole, and especially Mike Lee and Frank Gasparini. We are grateful to John Reppy for providing us with the data of Ref. [10]. This research was supported by NSF Grant No. DMR 90-13979.

[1] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973); J. M. Kosterlitz, J. Phys. C **7**, 1046 (1974).
[2] F. M. Gasparini and I. Rhee, in *Progress in Low Temperature Physics*, edited by D. F. Brewer (North-Holland, Amsterdam, 1992), Vol. XIII, Chap. 1.
[3] A. N. Berker and D. R. Nelson, Phys. Rev. B **19**, 2488 (1979); J. Tobochnik and G. V. Chester, *ibid.* **20**, 3761 (1979); S. A. Solla and E. K. Riedel, *ibid.* **23**, 6008 (1981); D. M. Ceperley and E. L. Pollock, *ibid.* **39**, 2084 (1989).
[4] Anopore available from Whatman Laboratory Div., 9 Bridewell Place, Clifton, NJ 07014.
[5] Millipore Corp., 80 Ashby Rd., Bedford, MA 01730.
[6] R. C. Furneaux, W. R. Rigby, and A. P. Davidson, Nature (London) **337**, 147 (1989).
[7] The membranes used in the first cell were 45 μm thick.
[8] See B. K. Bhattacharyya, M. J. DiPirro, and F. M. Gasparini, Phys. Rev. B **30**, 5029 (1984).
[9] G. P. Crawford *et al.*, J. Chem. Phys. **96**, 7788 (1992).
[10] D. F. McQueeney, Ph.D. thesis, Cornell University, 1988 (unpublished).
[11] P. Sullivan and G. Seidel, Phys. Rev. **173**, 679 (1969).
[12] L. M. Steele and D. Finotello, J. Low Temp. Phys. **89**, 645 (1992).
[13] L. M. Steele and D. Finotello (to be published).
[14] W. F. Saam and M. W. Cole, Phys. Rev. B **11**, 1086 (1975).
[15] G. Agnolet, D. F. McQueeney, and J. D. Reppy, Phys. Rev. B **39**, 8934 (1989).
[16] D. Finotello, Y. Y. Yu, and F. M. Gasparini, Phys. Rev. Lett. **57**, 843 (1986).
[17] L. M. Steele, C. J. Yeager, and D. Finotello, J. Low Temp. Phys. **89**, 661 (1992).
[18] P. W. Adams and V. Pant, Phys. Rev. Lett. **68**, 2350 (1992); M.-T. Chen, J. M. Roesler, and J. M. Mochel, J. Low Temp. Phys. **89**, 125 (1992).
[19] D. Finotello and F. M. Gasparini, Phys. Rev. Lett. **55**, 2156 (1985).
[20] D. Finotello, K. A. Gillis, A. Wong, and M. H. W. Chan, Phys. Rev. Lett. **61**, 1954 (1988).
[21] M. H. W. Chan, K. I. Blum, S. Q. Murphy, G. K. S. Wong, and J. D. Reppy, Phys. Rev. Lett. **61**, 1950 (1988).
[22] D. F. Brewer, J. Low Temp. Phys. **3**, 205 (1970).
[23] B. C. Crooker, B. Hebral, E. N. Smith, Y. Takano, and J. D. Reppy, Phys. Rev. Lett. **51**, 666 (1983).
[24] Y. Y. Yu, D. Finotello, and F. M. Gasparini, Phys. Rev. B **39**, 6519 (1989).
[25] A. J. Dahm, Phys. Rev. B **29**, 484 (1984).
[26] R. G. Petschek, Phys. Rev. Lett. **57**, 501 (1986).
[27] J. Machta and R. A. Guyer, J. Low Temp. Phys. **74**, 231 (1989), and references therein.
[28] V. Kotsubo and G. A. Williams, Phys. Rev. B **33**, 6106 (1986).
[29] M. Collins, G. Agnolet, W. M. Saslow, and E. Krotscheck, Phys. Rev. B **47**, 8905 (1993).
[30] Using ^{4}He bulk density, 1 liquid layer = 12.82 μmole/m^2.