

Fractal surface dimensionality and finite-size scaling at the superfluid transition of confined ^4He

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(Received 19 February 1985; revised manuscript received 18 September 1985)

A connection between surface fractal dimensionality and the critical behavior of confined ^4He at the superfluid transition is suggested. It is shown that in the specific case of Nuclepore filters the disagreement with bulk-correlation-length scaling can be resolved if one ascribes a fractal dimension to the confining surface of about 2.34. Explicit scaling functions for both the specific heat and the superfluid density are suggested. Measurements of adsorption isotherms for 0.2- μm filters support this fractal conjecture and yield a surface dimensionality of 2.24 ± 0.02 .

The behavior of ^4He at the superfluid transition has provided rather stringent tests for theoretical predictions of critical behavior. For both static and dynamic properties the agreement with theory has been excellent. This is true whether the transition takes place at saturated vapor pressure or at pressures up to the solidification point; or, equivalently whether the transition is in pure ^4He or in the presence of ^3He impurities.¹ This agreement with scaling and universality has one major exception. This is the situation where the helium is confined to a geometry whereby there are significant deviations from bulk behavior due to the limitations which the confinement imposes on the growth of the correlation length. In these circumstances, under the assumption that the confining surfaces do not affect the order parameter, scaling predictions² suggest a renormalization of the thermodynamic response in a way governed by the bulk correlation length. Experimentally this has proved not to be the case.

Measurements of heat capacity first suggested that the shift in the heat-capacity maximum and the value of the maximum did not scale in a proper way.³ In a subsequent analysis of these data, Gasparini, Chen, and Bhattacharyya (GCB) suggested a scaling function which allowed for a more detailed analysis of all these data, above and below the superfluid transition.⁴ This work reinforced the earlier conclusions which were based mostly on a single feature, the heat-capacity maximum. In this work it was also pointed out that correction-to-scaling terms needed to rectify this lack of scaling would have to be unphysically large.

More recently, Gasparini, Agnolet, and Reppy (GAR) analyzed data for the superfluid density of confined helium.⁵ It was found again that the bulk-correlation-length exponent did not yield the proper scaling. These authors were also able to suggest an expected relationship between the exponent which did scale the superfluid density and that which scaled the specific heat. This relationship was found to hold, thus greatly reinforcing the disagreement with the expected bulk-correlation-length scaling. The conclusions of the work of GCB and GAR were that either there is a new critical length associated with the surface, or that the surface affects the order parameter in an unexpected way.

In this paper it is suggested that a third possible explanation for the disagreement with bulk-correlation-length scaling is the roughness of the confining surface. What we mean is as follows. The thermodynamic behavior of a finite system, say a film, can be described not too close to the transition as a sum of a bulk free energy F_∞ and a surface free energy F_s ,

$$F \cong NF_\infty + N_s F_s, \quad (1)$$

where N is the total number of particles and N_s is the number at the surface. In the case of a planar surface, N_s is well defined, but, in the case of a rough surface, this is not so because the area with which N_s is associated is itself not uniquely defined. The area of a rough surface is larger the smaller the unit of area with which it is measured. Now, at the critical point, it is believed that there is only one critical length ξ . This length diverges near the bulk critical point T_c , as $\xi = \xi_0(1 - T/T_c)^{-\nu} = \xi_0 t^{-\nu}$, where ξ_0 is of atomic dimensions and ν a characteristic exponent. We suggest that near the critical point the surface area of a finite system is gauged by ξ^2 , thus the number of atoms "at the surface" becomes temperature dependent. Now for surfaces of arbitrary roughness, it is impossible to incorporate this idea quantitatively into the critical behavior. There is, however, a class of surfaces, those that have fractal dimension, for which this can be done. The concept of noninteger surface dimensionality D is associated with the fact that certain kinds of rough surfaces look invariant when viewed on different length scales.⁶ The area of these rough surfaces depend on the unit of measurement l^2 , as follows:

$$A(l) = A_0 l^{2-D}. \quad (2)$$

For planar surfaces $D=2$, thus A is a constant. For rough surfaces $D>2$ and $A(l)$ increases as l becomes small. For "earthlike" landscapes, for instance, D is found to be in the range of 2.1 to 2.4.⁶

We can now introduce the correlation length in Eq. (2) by using our ansatz that $l^2 \sim (\xi/\xi_0)^2$, thus

$$A \sim (\xi/\xi_0)^{2-D} = t^{\nu(D-2)}. \quad (3)$$

Thus, unless $D=2$, the boundary area which affects the

total thermodynamic response near the critical point is temperature dependent. For $D > 2$ this area becomes larger as one moves away from T_c . This behavior would explain why, in the case of the helium data, the effect of confinement extends much further out in t than would be expected on the basis of a fixed surface area and the temperature dependence of the bulk correlation length. What is suggested here is that this enhancement is due to the effective "growth" of the surface as it is probed with a smaller and smaller correlation length the farther one moves from the transition.

One can be more quantitative. GCB derive on the basis of Eq. (1) a scaling function for the difference between the bulk and confined helium specific heat, ΔC . This is given simply by

$$d\Delta C \sim t^{-\alpha_s}, \quad (4)$$

where d is the smallest average confinement size. With the assumption of bulk-correlation-length scaling one expects $\alpha_s = \alpha + \nu$. In the case of the superfluid density, GAR suggest the following scaling function:

$$[k - (\rho_s/\rho)t^{-\xi}]d^2 \sim t^{-(\xi - \xi_s)}, \quad (5)$$

where k is the amplitude of the power-law behavior of the bulk superfluid density and ρ_s/ρ is the superfluid density of the confined helium normalized by the total density. From scaling one has $\xi = \nu$, and on the basis of bulk-correlation-length scaling one expects $\xi - \xi_s = 2\nu$. Irrespective of the connection with the bulk-correlation-length exponent ν , however, GAR suggest that the following surface-bulk scaling relationship should hold:

$$2(\alpha_s - \alpha) = \xi - \xi_s. \quad (6)$$

In Fig. 1 are shown the data for the specific heat⁷ and the superfluid density⁸ of helium confined to the cylindrical pores of Nuclepore filters.⁹ These data are plotted in such a way as to test Eqs. (4) and (5). The heat capacity has two branches, one for $T < T_\lambda$ and one for $T > T_\lambda$. To the extent that the solid lines fitted to the data are parallel,¹⁰ this graph verifies the conjectured relation, Eq. (6). However, the slope expected from scaling with the bulk correlation length, which is indicated by the dashed line, is obviously steeper than the data. This then is the disagreement we wish to address.

To do so we assume that the inner pore surface of Nuclepore filters is rough and can be described as a fractal. We also note that the smallest confinement size d appearing in Eqs. (4) and (5) stems from the ratio of N/N_s , the total number of atoms to the number at the surface. This latter is proportional to the area A . Thus, in place of Eqs. (4) and (5) the following scaling equations follow from the derivations in Refs. 4 and 5:

$$d\Delta C \sim t^{-\alpha_s - \nu(2-D)}, \quad (7)$$

$$[k - (\rho_s/\rho)t^{-\xi}]d^2 \sim t^{-(\xi - \xi_s) - 2\nu(2-D)}. \quad (8)$$

Now by using the expected bulk-surface scaling relations $\alpha_s = \alpha + \nu$ and $\xi - \xi_s = 2\nu$ and the experimental results from the slope of the lines in Fig. 1,⁵ one can calculate the fractal surface dimensionality D . One finds for the two

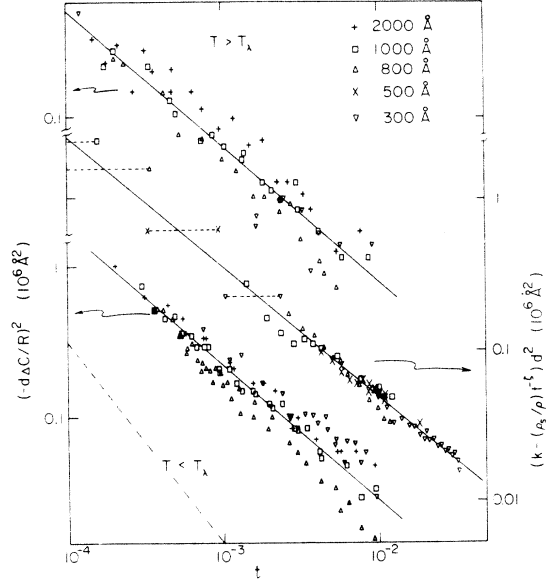


FIG. 1. Scaling of the two branches of the specific heat and the superfluid density of confined helium according to Eqs. (3) and (4). The gas constant R is used to normalize the specific heat. The various symbols indicate confinement in cylindrical pores of given diameter. The solid symbols refer to the specific-heat maximum. The symbols linked by a dashed line reflect the range of t allowed for the value of temperature where ρ_s vanishes (Ref. 8). The dashed line represents the expected slope of the data on the basis of bulk-correlation-length scaling.

branches of the specific heat $D = 2.30 \pm 0.02$ and 2.32 ± 0.03 for $T < T_\lambda$ and $T > T_\lambda$, respectively. In the case of the superfluid density one has 2.40 ± 0.02 . These numbers are in good agreement and seem reasonable when compared with the fractal dimensionality of surfaces obtained by Avnir, Farin, and Pfeifer.¹¹ These authors use adsorption measurements with different size molecules to find the value of D for different absorbers. For crushed glass, for example, they find $D = 2.35 \pm 0.11$, for porous silica gel 2.94 ± 0.04 , while for graphite 2.07 ± 0.01 . We also note that a Koch surface has a dimensionality of $2.26 \dots$ ¹²

We now examine more closely the assumption of roughness and fractal dimension for the Nuclepore filters. In Fig. 2 we show an electron micrograph of an $8\text{-}\mu\text{m}$ hole in a Nuclepore membrane.¹³ This hole is made by etching a radiation track in the polycarbonate membrane. The surface of interest is the one inside the hole. It is clear that this surface is rough, but it is certainly not obvious that it is fractal. To address this point we have followed the experimental procedure of Ref. 11 and measured adsorption isotherms with molecules of different effective cross-sectional areas σ . It follows from Eq. (1) that if one can establish the number of molecules to complete a monolayer on the adsorption surface N_1 , then

$$N_1 \sigma = A(\sigma) \sim \sigma^{(2-D)/2}. \quad (9)$$

Hence, by knowing σ one can extract D .

To make these measurements, we have chosen Nuclepore filters with $0.2\text{-}\mu\text{m}$ size holes. We have done this

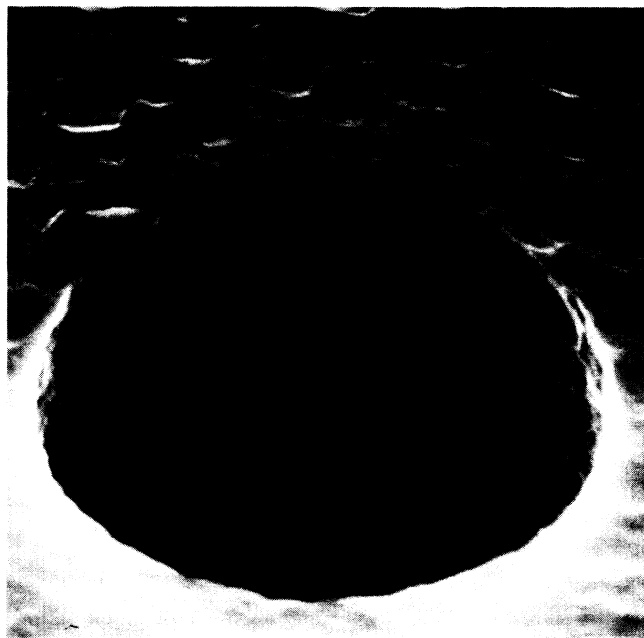


FIG. 2. Electron micrograph of an 8- μm pore in a Nuclepore filter membrane.

for several reasons. These particular filters have the largest area per filter and, equally important, have the largest percent of total surface within the holes. This is the surface to which the data of Fig. 1 are sensitive, hence it is the surface which is of interest. Further, we had studied these filters most extensively via N_2 and ^4He adsorption in the past. This gave us a good basis with which to check the new measurements for consistency.

The adsorption data were taken using a commercial surface-area analyzer.¹⁴ This consists of a vacuum system capable of 10^{-6} torr, two capacitance pressure sensors with a 40-torr and 1000-torr range, standard volumes, and a small-volume gas-handling manifold. The adsorption cell was similar to ones we have used in the past.¹⁵ It is a cylindrical brass can with 200 filter discs of 4.7 cm diameter. The spacing of the filters is a compromise to allow for gas promotion, hence, faster relaxation time, and for minimum gas volume. The adsorption isotherms obtained with this apparatus are shown in Fig. 3. Here we have plotted data for six different molecules ranging in effective area from 13.8 to 44.4 \AA^2 . These molecular areas

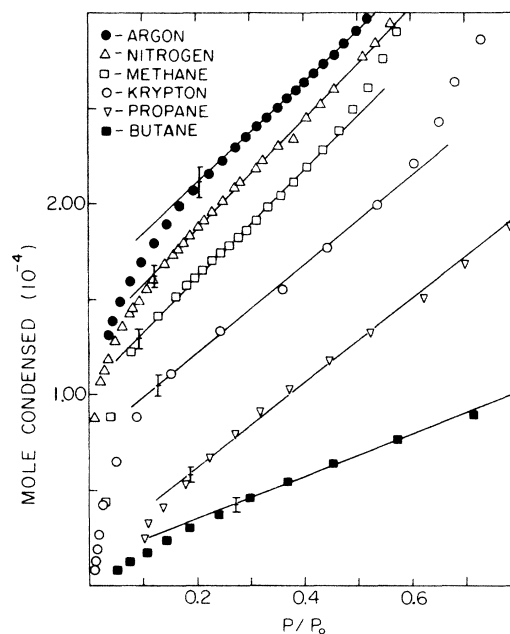


FIG. 3. Adsorption isotherms for 0.2- μm Nuclepore filters. The data for argon and nitrogen have been shifted up by 0.5 and 0.2×10^{-4} mole, respectively. The vertical bars indicate the uncertainty of the point *B* obtained as the point where the straight line deviates from the data at low coverage.

were calculated from the liquid bulk density at the temperature at which the isotherm was taken. To extract the monolayer coverage, we have attempted a Brunauer-Emmett-Teller (BET) analysis, but find that only argon and nitrogen yield reasonable agreement with the BET equation over a reasonable range of reduced pressure. Alternatively, we have used the "point-*B*" method to identify the monolayer coverage. This, as indicated in Fig. 3, is the point at which the isotherm begins to deviate more sharply from a near-rectilinear region.¹⁶ The results for the various adsorbates are given in Table I. From this we see that even though the range in molecular area is relatively narrow, there is a definite trend for the measured adsorption area to increase with decreasing molecular size. To test Eq. (9) we have plotted in Fig. 4 $\log_{10}(N_1\sigma)$ versus $\log_{10}\sigma$. The data define a reasonable straight line. We note that the nonzero slope is a measure of the deviation of the surface dimensionality from 2. We find from a

TABLE I. The surface area of 200 Nuclepore filter discs of 4.7 cm diameter and with 0.2- μm pores. The area is obtained using various adsorbates and the point *B* of the isotherm to identify monolayer completion.

Adsorbate	Molecular area (\AA^2)	Monolayer capacity (10^{-4} mole)	Isotherm temperature (K)	Area (m^2)
Argon	13.8	1.70 ± 0.08	77	14.2 ± 0.7
Nitrogen	16.2	1.40 ± 0.06	77	13.7 ± 0.6
Methane	17.8	1.24 ± 0.06	77	13.3 ± 0.6
Krypton	21.0	1.05 ± 0.04	77	13.3 ± 0.6
Propane	36.4	0.56 ± 0.04	195	12.3 ± 0.9
Butane	44.4	0.46 ± 0.03	77	12.3 ± 0.9

least-squares fit that $D = 2.24 \pm 0.02$. For comparison we have also shown on this plot a dashed line which corresponds to $D = 2.34$. This is a representative value of D as obtained from the finite-size scaling of the specific heat and the superfluid density. We believe that these values of D are reasonably consistent. In fact, one might even justify the slightly lower value of D for the $0.2\text{-}\mu\text{m}$ pore filters as opposed to filters with smaller size pores. The critical behavior data are for filters with pores in the 0.2- to $0.03\text{-}\mu\text{m}$ range, and it is observed that the smaller the pore size the rougher the surface.¹⁷ Thus, the present adsorption data should yield a lower value of D than the ones obtained from the critical behavior.

Lastly, we point out that in the work of GAR several other sets of data for the superfluid density are analyzed. Among these are data taken with helium confined between sheets of Mylar.¹⁸ The surface of this material is substantially smoother than the surface associated with the Nuclepore filters. One would expect on this basis that the fractal dimensionality for these data would be closer to 2. One finds indeed that $D = 2.12 \pm 0.04$.

In summary, we have presented in this paper a conjecture that surface roughness modifies the behavior of a finite-size system near the critical point. This effect is in addition to the expected effects of finite-size scaling which can be described via an average smallest confinement size. In the specific case of helium confined in pores of Nuclepore filters, we have shown that if the confining surface of the pores is fractal, then one can work out explicit scaling functions for the specific heat and the superfluid density. One finds that one requires $D \cong 2.34$ to have agreement with predictions of bulk-correlation-length scaling. In an independent determination of D for

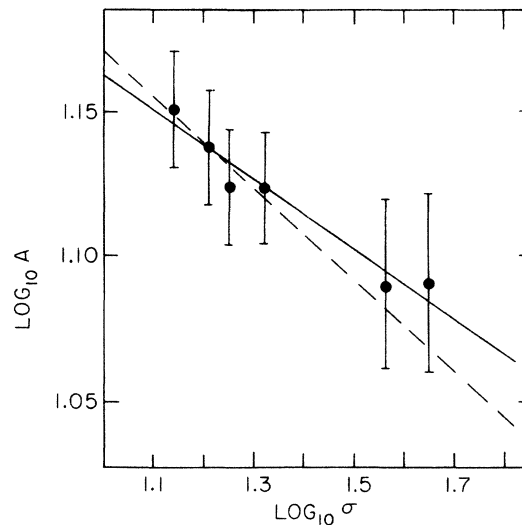


FIG. 4. The log of the adsorption area versus the log of the molecular area of the adsorbate. The solid line is a least-squares fit. The dashed line represents a slope of 2.34.

$0.2\text{-}\mu\text{m}$ filters via adsorption isotherms, we find $D = 2.24 \pm 0.02$. This supports our conjecture of the fractal nature of the surface and its effect on critical behavior.

We are grateful to H. W. Ballew of Nuclepore Corp. for making the micrograph shown in Fig. 2 available for publication. This work is supported in part by the National Science Foundation, Low Temperature Physics, Program, Grant No. DMR-83-05742.

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²M. E. Fisher, in *Critical Phenomena*, Course 51 of *Proceedings of the International School of Physics, "Enrico Fermi,"* edited by M. S. Green (Academic, New York, 1971). For a recent review, see M. N. Barber, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983).

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⁶B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1982).

⁷These are the same data as in Refs. 3 and 4. Tar-pin Chen, Ph.D. thesis, State University of New York at Buffalo, 1977.

⁸J. S. Brooks, B. B. Sabo, P. C. Schubert, and W. Zimmermann, Jr., *Phys. Rev. B* **19**, 4524 (1979).

⁹Nuclepore Corporation, 7035 Commerce Circle, Pleasanton, California 94586.

¹⁰These lines should actually be parallel only to the extent that $\alpha = 0$. With $\alpha \cong -0.02$ one has about a 2% correction.

¹¹D. Avnir, D. Farin, and P. Pfeifer, *J. Chem. Phys.* **79**, 3566 (1983).

¹²P. Pfeifer and D. Avnir, *J. Chem. Phys.* **79**, 3558 (1983).

¹³Nuclepore Corporation, Ref. 9. We are grateful to H. W. Ballew for making this photograph available.

¹⁴Model 2100D, Micromeritics Instruments Corporation, Norcross, Georgia.

¹⁵T. P. Chen, M. J. Di Pirro, B. K. Bhattacharyya, and F. M. Gasparini, *Rev. Sci. Instrum.* **51**, 846 (1980).

¹⁶Of the two isotherms which could be analyzed with the BET equation, nitrogen and argon, the first yielded an area of $13.4 \pm 0.6 \text{ m}^2$, while the latter 11.7 m^2 . Thus, as can be seen from Table I, nitrogen is in excellent agreement with the point-B determination, while argon is not. We do not understand this discrepancy.

¹⁷In Ref. 14 it is shown that the smaller the size of the pores the greater the ratio of adsorption area to geometrical area. This is consistent with a rougher surface for the smaller size pores.

¹⁸Mylar is a trade name registered to the E. I. Dupont de Nemours Company, Inc.

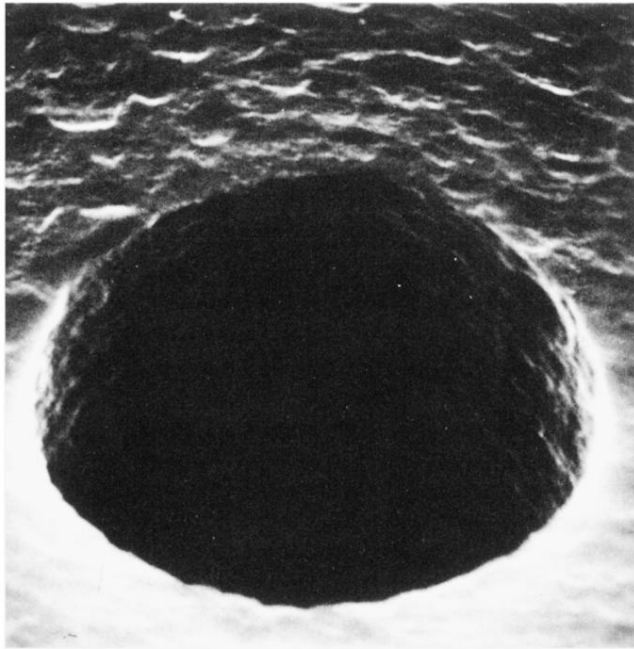


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