tals, Ing. L. H. M. Coenen for valuable assistance during the measurements, and Professor J. F. Carolan for critical reading of the manuscript. Part of this work has been supported by the Strichting voor Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO).

[1]R. Nathans, F. Menzinger, and S. J. Pickart, J. Appl. Phys. 39, 1237 (1968).

[2]R. J. Birgeneau, J. Shalyo, and G. Shirane, J. Appl. Phys. 41, 1303 (1970).

[3]M. T. Hutchings, G. Shirane, R. J. Birgeneau, and S. L. Holt, Phys. Rev. B 5, 1999 (1972).

[4]L. J. de Jongh and A. R. Miedema, Adv. Phys. 23, 1 (1974).

[5]J. H. M. Stoelinga and P. Wyder, J. Chem. Phys. 61, 478 (1974), and 64, 4612 (1976).

[6]L. H. M. Coenen, H. N. De Lang, J. H. M. Stoelinga, H. van Kempen, and P. Wyder, Solid State Commun. 20, 713 (1976).

[7]F. W. Gorter, L. J. Noordermeer, A. R. Kop, and A. R. Miedema, Phys. Lett. 29A, 331 (1967); F. W. Gorter, thesis, University of Amsterdam, 1969 (unpublished).

[8]P. Bloembergen and A. R. Miedema, Physica (Utrecht) 75, 205 (1974); P. Bloembergen, Physica (Utrecht) 85B, 51 (1977).

[9]A. R. Miedema, P. Bloembergen, J. H. P. Colpa, F. W. Gorter, L. J. de Jongh, and L. J. Noordermeer, in *Magnetism and Magnetic Materials—1973*, edited by C. D. Graham, Jr., and J. J. Rhyne, AIP Conference Proceedings No. 18 (American Institute of Physics, New York, 1974), p. 806.

[10]W. Marshall, in *Proceedings of the Conference on Critical Phenomena*, National Bureau of Standards Miscellaneous Publications No. 273 (U. S. GPO, Washington, D. C., 1965).

[11]K. Kawasaki, Prog. Theor. Phys. 29, 801 (1963).

[12]N. A. Lurié, D. L. Huber, and M. Blume, Phys. Rev. B 9, 2171 (1974).

[13]D. Walton, J. E. Rives, and O. Khalid, Phys. Rev. B 8, 1210 (1973).

[14]D. J. Saunders and D. Walton, Phys. Rev. B 15, 1489 (1977).

Superfluid-Vortex Thresholds and the Vortex-Core Parameter near T_λ

I. H. Lynall, D. S. Shenk, R. J. Miller, and J. B. Mehl
Physics Department, University of Delaware, Newark, Delaware 19711

(Received 20 May 1977)

Superfluid-vortex thresholds in a rotating annulus were detected with second sound in the temperature range $0.01\text{ K} < T_\lambda - T < 0.2\text{ K}$. A rapid decrease of the threshold angular velocity ω_{c1} was observed as $T \to T_\lambda$. The data can only be fitted to the theory of Fetter if a rapidly diverging vortex-core parameter is assumed.

Numerous investigators[1-3] have shown that experimental values of ω_{c1}, the threshold angular velocity for equilibrium vorticity in a rotating container of liquid helium, are in good agreement with the predictions of Fetter.[4] In addition, the growth of vorticity above ω_{c1} in a rotating annulus has been shown[5] to be in good agreement with the theory of Stauffer and Fetter.[6] All of these investigations were made at temperatures between 1.2 and 1.8 K. In this Letter we report measurements of ω_{c1} in a rotating annulus at temperatures near the superfluid phase transition ($0.01\text{ K} < \Delta T < 0.2\text{ K}$; $\Delta T = T_\lambda - T$). The results are of interest because a rapid decrease of ω_{c1} with increasing temperature has been observed. The data can be fitted by Fetter's formula only if a rapidly diverging core parameter is assumed, which attains values near T_λ which are appreciably larger than generally assumed.

Fetter predicted, using a thermodynamic argument, that for a thin annulus of width D and mean radius R, the threshold is given by

$$\omega_{c1} = \frac{\kappa}{\pi D^2}\left(\ln\frac{2D}{\pi a}\right)\left(1 - \frac{D}{6R}\right), \tag{1}$$

where $\kappa = h/m_{\mathrm{He}}$ is the quantum of circulation and a is the vortex-core parameter.[7] The core parameter is generally assumed to be on the order of 1 Å well below T_λ. Vortex-ring experiments have been used to determine a at low temperatures.[8,9] Between 0.3 and 0.6 K (at saturated vapor pressure) a increases from 1.25 Å to 1.35 Å; the total increase upon pressurization to the melting line is ~30%. At higher temperatures, there are no precise measurements. It is often assumed that a is proportional to the "healing length" near T_λ, and hence that it diverges as $t^{-2/3}$, where $t = \Delta T/T_\lambda$.[10] A search for this divergence was one of the goals of the present work.

Vorticity thresholds were determined using second sound as a probe of vorticity.[2] The dissipative interaction between second sound and vortex lines causes an increase of the resonance width. Measurements of the width as a function of the angular velocity ω were used to detect the onset of steady-state vorticity at ω_{c1}.

Three annular second-sound resonators were used. Annulus A is constructed of borosilicate glass; it has an inner radius of 0.876 cm, a width of 0.0762 cm, and a height of 1.7 cm. Boronnitride end pieces held the cylinders concentric. Eight equally spaced 0.8×0.8 mm^2 slots were cut at each end of the inner cylinder for electrical leads and for conduction of heat from the resonator. The multistrand leads were passed through the slots, fanned out, and potted with silver paint. Eight parallel carbon-film strips were sprayed on this cylinder, contacting the silver paint at each end. The resistances of the films were uniform to within about 10%. Combinations of the films were used as transducers for generating and detecting second sound.

Annuli B and C were machined from a glass-ceramic.[11] A common inner cylinder with a radius of 1.013 cm was used. Interchangeable outer parts were used to make annuli with widths of 0.0798 cm (B) and 0.0644 cm (C), and heights of 2.0 cm. Sixteen small holes near the ends of the inner cylinder were used for electrical leads. The holes were filled with silver paint, leaving a smooth inner surface. Sixteen 1-mm-diam holes in the outer cylinder provided for conduction of heat from the resonator. Carbon films were applied and used as with annulus A. Although annuli B and C have cleaner inner geometries than annulus A, no important acoustic or hydrodynamic differences were observed in their use.

The remainder of the apparatus has been previously described.[5] The resonators were mounted in a protective can in the helium bath, which was regulated to better than 3 μK. Small holes in the can provided thermal contact with the bath. The low-level electronics were rotated and coupled to the stationary electronics through a rotary transformer.

The second-sound modes of an annulus can be described by a temperature variation $T'\propto\varphi_{ns}(kr)\times\cos(s\theta)$, where φ_{ns} is a linear combination of Bessel and Neumann functions. (Modes with a component of the relative velocity $\vec{v}_n-\vec{v}_s$ parallel to the annulus axis are neglected here.) For the lowest-frequency modes of a thin annulus, φ_{ns} is approximately tangential, and the frequencies correspond to the condition that s wavelengths fit into a mean circumference. In the present work, the mode with $n=0$ and $s=4$ was used. This mode has the advantage of insensitivity to geometric perturbations, and to the perturbations arising from the Coriolis effect and the B' term of Hall and Vinen.[12] These perturbations vanish in the limit where φ_{ns} is constant. Numerical calculations show that these perturbations, which split the angular degeneracy, are unimportant and unobservable in this work. No splitting was in fact observed.

The $s=4$ mode was excited by driving four alternately spaced transducers in parallel at half the resonance frequency. One or more of the remaining transducers was biased with a constant current and used as a detector. The second-sound amplitude was observed as an ac-voltage across the detector. The signal amplitude A was measured at a number of frequencies $\sigma/2\pi$ near the resonance frequency $\sigma/2\pi$. The results were fitted to a Lorentzian function $A=A_0[1+(\sigma-\sigma_2)^2\gamma^{-2}]^{-1}$. The resonance half-width at half-maximum γ as well as the other resonance parameters was determined in the fitting. The rms deviation from a Lorentzian shape was typically 0.05%, comparable with the instrumental resolution.

For annulus A the resonance frequencies $\sigma_0/2\pi$ varied between 1140 Hz at $\Delta T=0.2$ K and 400 Hz at $\Delta T=0.01$ K; over the same temperature range $\gamma_0/2\pi$ varied from 1.5 to 0.25 Hz. Here γ_0 is the half-width in the absence of rotation. These widths are comparable with those of the radial modes[5] although the Q's for the latter case ($Q=\omega/2\gamma$) are much larger, because of the larger ω. Numerical data for the other annuli are similar, aside from expected geometric effects.

The drive power was kept below a critical level, below which γ_0 was constant within experimental accuracy. The critical power varied between ~ 20 μW at $\Delta T=0.01$ K to ~ 500 μW at $\Delta T=0.2$ K for annulus A, with similar results for annuli B and C. The critical power was independent of rotation. No critical-power effects were observed for the detectors. The power level of these was arbitrarily set equal to that of the drive transducers. All data taken here were taken at power levels at least 2 dB below the critical levels. Partly as a result of the lower critical power, the working signal was weaker at

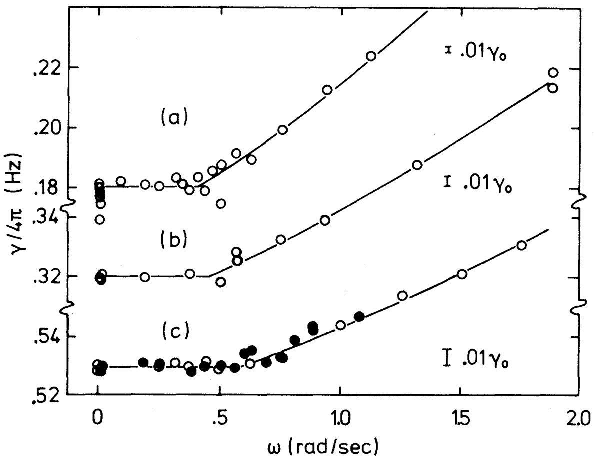

FIG. 1. Resonance half-width at half-maximum γ vs angular velocity ω for annulus A at $\Delta T = 0.022$ K (a), 0.050 K (b), and 0.100 K (c). The closed symbols in c were taken at a drive power 3 dB lower than the open symbols. The curves are fits to Eq. (2) with $\omega_{c1} = 0.42$, 0.46, and 0.58 rad/sec; and $B = 2.4$, 1.81, and 1.38 for a, b, and c, respectively.

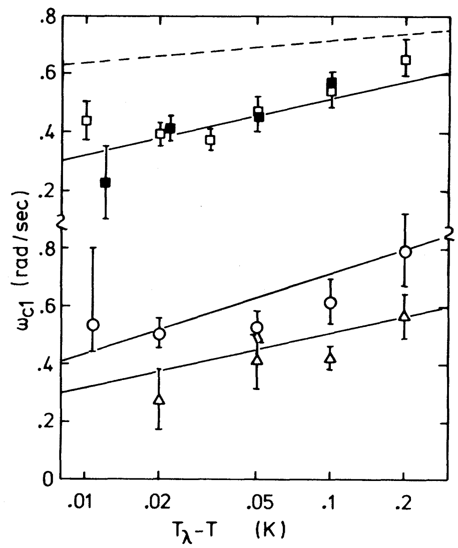

FIG. 2. Vorticity threshold ω_{c1} vs $T_\lambda - T$ for annuli A (squares), B (triangles), and C (circles). The closed squares were taken with drive power 3–6 dB higher than the open-square data at the same temperatures. The indicated uncertainties are standard errors. The solid lines are computed from Eq. (1) with $a = (2.7\ \text{Å})t^{-1.58}$; the dashed line is for annulus A with $a = (1\ \text{Å})t^{-2/3}$.

higher temperatures. This limited work to $\Delta T > 0.01$ K.

The dependence of γ on angular velocity ω is shown for annulus A at three temperatures in Fig. 1. The resonance half-width γ is independent of ω at low ω, and increases above a threshold ω_{c1}. Below 2.1 K, following a change in ω, the value of γ stabilized after about 10–20 min. A delay of 30–60 min was generally allowed, which resulted in reproducible, hysteresis-free data. Above about 2.1 K, nonequilibrium states with both excess and deficient vorticity could be observed for long periods of time. Accordingly, a technique which led to equilibrium states in other experiments was used.[3,13] The system was warmed above T_λ, rotated steadily for a few minutes, and cooled in rotation. Data were taken after the temperature was again carefully stabilized. This technique was used in the ion experiment of DeConde and Packard,[3] who used cooling in rotation to 1.2 K, where single-vortex thresholds corresponding to $a \simeq 1$ Å were observed. In the present work, this technique led to reproducible data at working temperatures near T_λ. Unfortunately, because of practical difficulties, it was not possible to use this procedure at the lower temperatures.

The curves in Fig. 1 were determined by fitting the data by

$$\gamma = \begin{cases} \gamma_0, & \omega \leq \omega_{c1}, \\ \gamma_0 + \frac{1}{2}B\omega[1-(\omega_{c1}/\omega)^{1/2}], & \omega > \omega_{c1}, \end{cases} \tag{2}$$

where B is the Hall-Vinen parameter,[12] and the correction term in brackets is just the fraction of the area occupied by vortices. It is determined by noting that a vortex-free region of width $\Delta R \propto \omega^{-1/2}$ is expected near the walls; and that $\Delta R = \frac{1}{2}D$ at the threshold.[6] Here, in contrast to previous work,[5] $\vec{v}_n - \vec{v}_s$ is uniform across the annulus, leading to a much simpler expression for γ.

Values of ω_{c1} determined from fits of our data by Eq. (2) are shown in Fig. 2 as functions of ΔT. In all cases the values of B obtained in the fits were consistent with published data.[14] No power dependence was observed; the solid squares correspond to data taken at power levels of 3–6 dB higher than the corresponding open symbols. Similar values of ω_{c1} were found if the data were fitted with a straight line for $\omega > \omega_{c1}$ instead of with Eq. (2), or if the thresholds were simply read off plots similar to Fig. 1. The dashed line in Fig. 2 corresponds to Eq. (1) with $a = (1\ \text{Å})t^{-2/3}$; this divergence is clearly too weak to account for the data.

Values of the core parameter calculated direct-

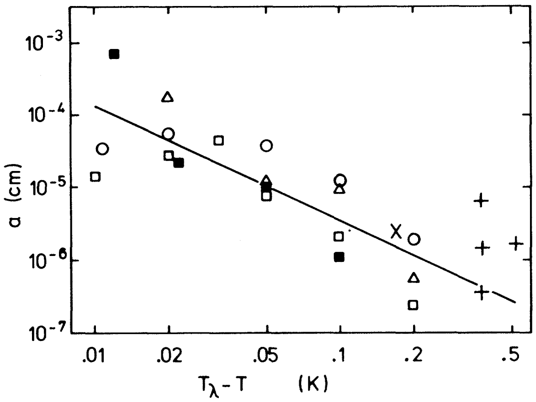

FIG. 3. Values of a calculated from the data in Fig. 2, except for plusses (Ref. 5) and cross (Ref. 15). The solid line is the best fit $a = (2.7\ \text{Å})t^{-1.58}$.

ly from the data in Fig. 2 using Eq. (1) are shown in Fig. 3. The large scatter is due to the logarithmic dependence of ω_{c1} on a. A rapid divergence is observable, however, and even at the lowest temperatures the values of a are quite large. For comparison, values of a from other experiments are included. The plus symbols correspond to values of ω_{c1} determined in much larger annuli,[5] and the cross symbol was determined from film-flow data.[16] The best fit of the data from the present work by $a = a_0 t^{-x}$ gives $a_0 = 2.7 \pm 1.4$ Å and $x = 1.58 \pm 0.13$. These parameters were used to calculate the solid lines in Figs. 2 and 3, which show that all the ω_{c1} data are reasonably consistent with this expression for a. We conclude that the ω_{c1} data can only be fitted to Eq. (1) if an expression for a which diverges much more rapidly than is generally assumed is used. In particular, our expression for a diverges much more rapidly than the superfluid healing length,[10] the transverse correlation length,[15] and the length determining critical dynamics near T_λ,[17] all of which diverge approximately as $t^{-2/3}$. It is possible that a superfluid structure with a $t^{-2/3}$ length dependence is masked by a complex excitation structure whose size determines a.[18] It is interesting to note that our expression for a predicts that the total core area will be equal to the total sample area at $\omega \simeq \omega_{c2} = 20$ rad/sec at $\Delta T = 1$ mK. A transition to a "normal" state under these conditions may be observable. Similarly, our expression for a can account for the approximate magnitude of the λ-point depressions which have been observed in some (but not all) heat-flow experiments.[19]

An interpretation of the data as indicating a diverging core parameter is dependent on the applicability of Eq. (1). This expression is not strongly geometry dependent; in an elongated elliptic cylinder with minor axis D, an elongated rectangle with width D, or in the annulus with width D, the first vortex occurs at the angular velocity given by Eq. (1) if the correction term $(1 - D/6R)$ is omitted.[20] This correction term takes into account the effect of finite annulus width to first order; this correction is small and temperature independent. Hence the possibility of finding theoretical thresholds lower than Eq. (1) and/or consistent temperature-dependent deviations are probably limited to arrays of nonparallel vortices, a difficult theoretical problem. Experimental studies in other geometries (e.g., with a variable length along the rotation axis) may help clarify this.

The authors gratefully acknowledge the support of the National Science Foundation (Grant No. DMR 72-00184 A01).

[1]G. B. Hess and W. M. Fairbank, Phys. Rev. Lett. 19, 216 (1967).

[2]P. J. Bendt and R. J. Donnelly, Phys. Rev. Lett. 19, 214 (1967); P. J. Bendt, Phys. Rev. 164, 262 (1967).

[3]K. DeConde and R. E. Packard, Phys. Rev. Lett. 35, 732 (1975).

[4]A. L. Fetter, Phys. Rev. 153, 285 (1967).

[5]D. S. Shenk and J. B. Mehl, Phys. Rev. Lett. 27, 1703 (1971), and in *Low Temperature Physics—LT 13*, edited by N. J. O'Sullivan, K. D. Timmerhaus, and E. F. Hammel (Plenum, New York, 1974), p. 314.

[6]D. Stauffer and A. L. Fetter, Phys. Rev. 168, 156 (1968).

[7]A. L. Fetter, Ref. 4, and private communication. The correction term $D/6R$ is on the order of 1% for the annuli used here.

[8]G. W. Rayfield and F. Reif, Phys. Rev. 136, A1194 (1964).

[9]M. Steingart and W. I. Glaberson, J. Low Temp. Phys. 8, 61 (1972).

[10]G. G. Ihas and F. Pobell, Phys. Rev. A 9, 1278 (1974), and references therein.

[11]Macor, Corning Glass Works, Corning, N. Y.

[12]H. E. Hall and W. F. Vinen, Proc. Roy. Soc. London, Ser. A 238, 204, 215 (1956).

[13]J. B. Mehl and W. Zimmermann, Jr., Phys. Rev. 167, 214 (1968).

[14]P. Mathieu, A. Serra, and Y. Simon, Phys. Rev. B 14, 3753 (1976), and references therein.

[15]P. C. Hohenberg, A. Ahorony, B. I. Halperin, and E. D. Siggia, Phys. Rev. B 13, 2986 (1976).

[16]R. B. Hallock (private communication) finds that data, although preliminary, similar to those in Fig. 6 of R. B. Hallock and E. B. Flint [Phys. Rev. A 10,

1285 (1974)], are best fitted to a vortex-pair model. Such fits yield a core parameter of 250 Å at 2.01 K.

[17]C. Buchal and F. Pobell, Phys. Rev. B 14, 1103 (1976); R. Carey, C. Buchal, and F. Pobell, to be published.

[18]W. I. Glaberson, J. Low Temp. Phys. 1, 289 (1969).

[19]See, e.g., S. M. Bhagat and R. S. Davis, J. Low Temp. Phys. 7, 157 (1972); P. Leiderer and F. Pobell, Z. Phys. 273, 378 (1969).

[20]A. L. Fetter, J. Low Temp. Phys. 16, 533 (1974).

Critical Behavior of a Binary Mixture of Protein and Salt Water

Coe Ishimoto
Department of Biology, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

and

Toyoichi Tanaka
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 31 May 1977)

Evidence is presented for the existence of a critical mixing point of a protein and salt-water binary mixture. The asymptotic behavior of the osmotic isothermal compressibility and the long-range correlation length near the critical mixing point is consistent with the scaling laws predicted by the mean-field theory. The dynamic behavior of concentration fluctuations is not described by the mode-coupling theory.

The universality of the asymptotic behavior of certain equilibrium and transport thermodynamic properties of binary mixtures near the critical mixing point has been well established over the previous decade.[1,2] In this Letter we present evidence for the existence of a critical binary mixture of a globular protein, lysozyme (molecular weight: 14 388), and a 0.5*M* aqueous solution of NaCl (*p*H 5.4). An understanding of critical behavior, and more generally of phase transitions, in protein/solvent mixtures is of considerable interest as a new physico-chemical approach to the study of protein solubility. It is also of great physiological importance in relation to the phenomenon of cold cataract in certain animal lenses.[3,4] The lysozyme molecule is approximately ellipsoidal, with dimensions of $45\times 30 \times 30$ Å^3.[5] The dimensions of the individual molecules of the two components in a binary mixture of lysozyme and salt water are thus different by as much as an order of magnitude. The lysozyme molecule carries 6.5 net positive electrical charges at *p*H 5.4.[6] Such a mixture of compact globular macromolecules and solvent, or a mixture in which one of the components carries net electrical charges, has not previously been investigated as a critical binary mixture. The salt water is treated as a single component although it contains Na^+ and Cl^- ions as well as water molecules. The salt is required for the critical temperature to be in the range between the freezing point of the mixture (approximately -10°C) and the denaturation temperature of lysozyme (approximately 55°C).[7]

We investigated the asymptotic behavior near the critical mixing point of the osmotic isothermal compressibility and the long-range correlation length by measuring the turbidity of the mixture along the critical isochore. The behavior of these equilibrium thermodynamic properties was found to be consistent with the behavior predicted by the mean-field theory[8] (critical exponents $\beta = \frac{1}{2}$, $\gamma = 1$, $\nu = \frac{1}{2}$). The macroscopic shear viscosity showed a large divergence near the critical mixing point; its relationship to the decay rate of concentration fluctuations was not in agreement with the prediction of the mode-coupling theory.[9]

Crystalline flakes of chicken-egg-white lysozyme (3.2.1.17, Worthington; specific activity: 11 700 units) were dissolved in a 0.5*M* aqueous solution of NaCl (Mallinckrodt, reagent grade, dissolved in distilled water) with precautions taken to avoid denaturation of the protein. The dissolved mixture was centrifuged at 1500*g* for 5 min in order to remove air bubbles and the small amount of undissolved protein. The volume fraction of protein was determined from a measurement of OD_{280}, after $\times 1000$ dilution in water, the extinction coefficient of lysozyme, $E_{1\,\mathrm{cm}}^{1\%} = 26.4$, and the partial specific volume of lysozyme, $\bar{v} = 0.703$. This volume fraction was divided by a factor of 0.74, so that 100% corresponds to the close-packed arrangement in which the shape of