Meetings

Critical-Point Phenomena

The critical point of the liquid-vapor phase transition, the so-called second order phase transitions, the Curie point and Néel points in magnetism, and the λ-point of the superfluid transition in liquid helium are all examples of phenomena in the neighborhood of critical points. The fact that there may be a common basis for such diverse phenomena was discussed at a conference at the National Bureau of Standards, Washington, D.C., 5–8 April 1965. About 200 physicists and chemists attended, representing such fields as classical *PVT* measurement, low-temperature calorimetry, nuclear and paramagnetic resonance, light x-ray and neutron scattering, and the measurement of ultrasonic propagation.

The critical point of the liquid-vapor phase transition was studied extensively both theoretically and experimentally by van der Waals toward the end of the 19th century. His equation of state and his principle of corresponding states form important conceptual tools in the liquefaction of so-called permanent gases which took place around that time. The dramatic phenomenon of critical opalescence in which the enormous critical density fluctuations make themselves manifest through the scattering was studied theoretically by Ornstein and Zernike in the beginning of the 20th century. A historical review of these investigations, as well as those of Curie and Weiss in magnetism and Bragg and Williams in order-disorder phenomena, was delivered by George Uhlenbeck (Rockefeller Institute). Uhlenbeck emphasized the underlying similarity in all these theories. He pointed out that although van der Waals theory of the equation of state, and also the parallel theories of Weiss and Bragg-Williams, has been considered quite unrigorous and of purely heuristic value, it is in fact a rigorous theory in the limit of weak long-range forces. These theories thus give the major features of the phenomena although they cannot describe the immediate neighborhood of the critical point. A similar point was made by Michael Fisher with respect to the Ornstein-Zernike theory of critical opalescence.

One of the motivations of the conference was the growing evidence, both experimental and theoretical, that in the immediate neighborhood of the critical point, thermodynamic potentials are not analytic functions of the parameters describing the system. This contradicts the classical theories. The experimental data relevant to this question for liquid vapor and binary liquid mixture systems was reviewed by J. S. Rowlinson (Imperial College, London). The most unequivocal instance of deviations from the predictions of the classical theory is the shape of the coexistence curve. Experimental data can be represented in the form

$$(\rho_l - \rho_g)/\rho_c = D\,(\Delta T/T_c)^\beta \qquad (1)$$

where ρ_g is the density of the gas, ρ_l the density of the liquid, ρ_c and T_c the density and temperature of the critical point, ΔT the deviation of the temperature from the critical temperature, and D and β are constants. The classical theories predict a value for β of ½, whereas the best experimental value of β for most gases is very close to ⅓. A value of β of approximately ⅓ also describes the data for the shape of the consolute curve for the binary liquid mixture. Rowlinson also discussed data on the shape of the critical isotherm, the dependence of the compressibility on the temperature, and the dependence of the specific heat at constant volume on the temperature. These can also be represented in a form similar to Eq. 1. In these cases, too, they differ from the classical values. Two rigorous inequalities among these exponents have been derived thermodynamically by Rushbrooke and Griffiths. Rowlinson concluded from these inequalities that the exponent α which describes the behavior of the specific heat can probably be assigned a small positive value.

One of Rowlinson's conclusions is that the experimental data on gases and binary liquid mixtures obtained by the usual *PVT* and calorimetric techniques are not accurate enough to decide the delicate questions of the neighborhood of the critical point. An experimental method which has more promise for accurate measurement of *PVT* data very near the critical point was described by Ernst Schmidt (Technische Hochschule, Munich). This method takes advantage of the fact that gravity causes large density gradients to be set up in a gas near the critical point. These density gradients can be directly related to the equation of state and can be measured by the deflection of a beam of light which passes through the nonuniform gas. The method clearly shows that the density gradients observed are much larger than those which would be predicted by classical theory, but it has not yet been exploited to yield the maximum quantitative information. A similar experimental investigation for binary liquid mixtures was described by H. L. Lorentzen (University of Oslo). Lorentzen also applied this method for the investigation of the very slow approach to equilibrium near the critical point.

Two review papers dealt with critical phenomena in magnetism. Cyril Domb (King's College, London) reviewed lattice theories of magnetism and gases, and George Benedek (Massachusetts Institute of Technology) reviewed experimental results on equilibrium properties of ferro- and antiferromagnets. Domb discussed the results obtained by evaluating quite long sequences of terms (of the order of 10 or 20 members) of the rigorous high- and low-temperature expansions for the thermodynamic properties of various lattice models. The obtaining of these coefficients is quite an achievement because the higher terms are quite complicated and cannot be evaluated without using ingenious graphical relations. These series are summed by several different methods and yield very accurate information about the critical parameters and the exponents describing the trend of various quantities near the critical point.

Although ferro- and antiferromagnetism appear to be very different from the liquid-vapor phase transition or the phase transition of a binary liquid mixture, they have very similar descriptions in statistical thermodynamic theory and it is possible to make a "dictionary" which permits the translation from the magnetic to the liquid-vapor use and vice versa. Magnetization thus corresponds to difference between the densities of the liquid and vapor phases; susceptibility corresponds to compressibility and the relation of the magnetic field to magnetization corresponds to the relation of the pressure to volume in a gas. Benedek's talk was thus concerned with the same "exponents" as Rowlinson's. Perhaps the most striking feature of the magnetic experimental data is the fact that the coefficient β which describes the magnetization curve is very close to $1/3$. This result was obtained in a classic experiment by Heller and Benedek by using the nuclear magnetic resonance frequency as a probe of the internal field.

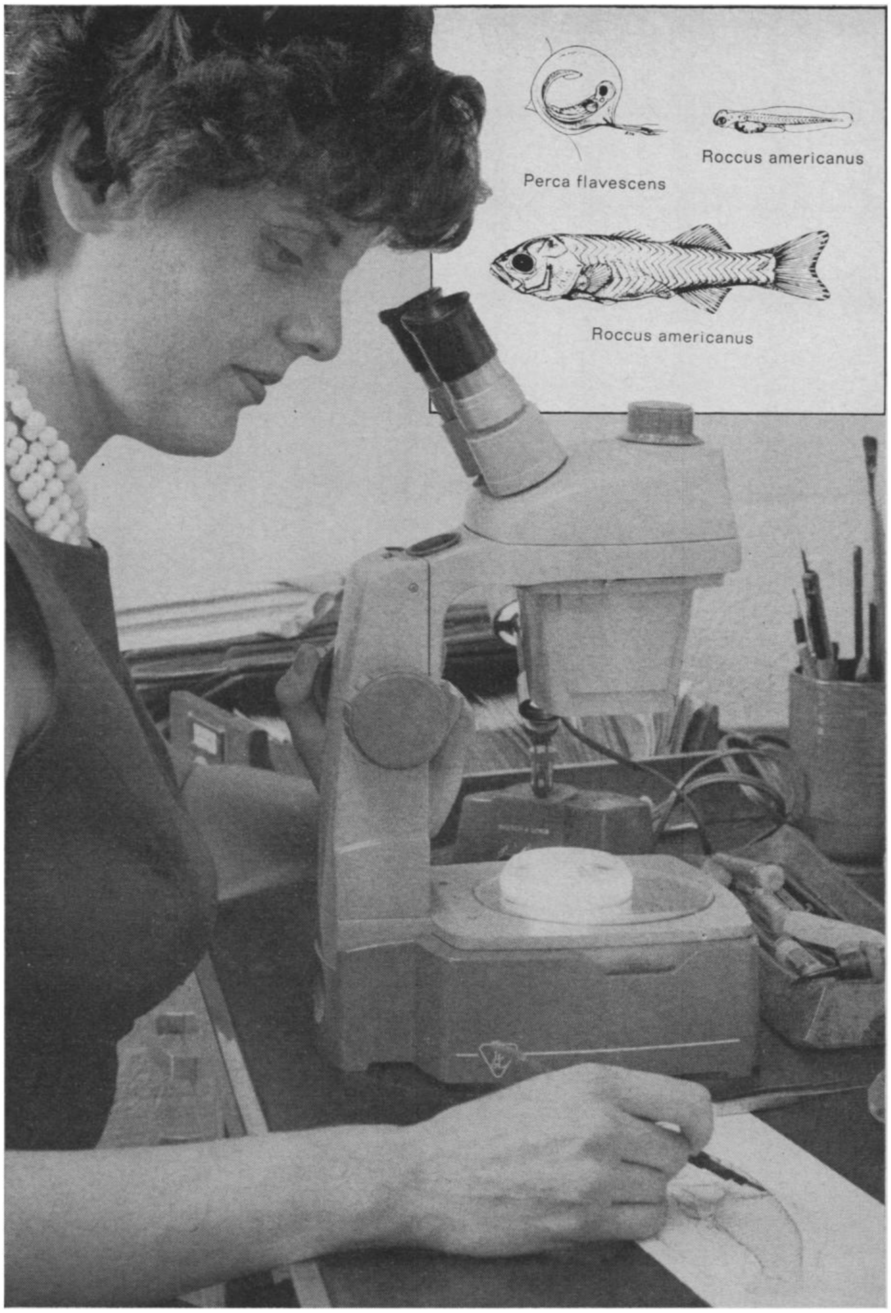
Recent work as well as recent analysis of old experimental work indicates also that the Curie-Weiss law for the susceptibility must be replaced by a minus 4/3 power law. Both of these experimental results are in very good agreement with the predictions of the series summation method for the Heisenberg ferromagnet. Other discussions on magnetism were by Werner Wolf (Yale University) on the critical properties of a magnetic system which closely resembles the Ising model; Dale Teaney (IBM) on the specific heat of ferro- and antiferromagnets, and Peter Heller (Brandeis University) on the line widths of the nuclear magnetic resonances in ferro- and antiferromagnets.

A question which came up from time to time was whether the logarithmic singularity in the specific heat at constant volume for the λ-point of helium is a universal feature of all phase transitions. The interest of this question was enhanced by the experiments of A. V. Voronel (University of Kharkov) on the specific heat at constant volume of oxygen and neon, and of M. E. Moldover and W. A. Little (Stanford University) on helium, near their critical points. Both experiments indicated that the specific heat of oxygen, neon, and helium can be fitted very well by a logarithmic curve. W. Fairbank reviewed data on the helium λ-point, and Moldover presented results on the critical point of helium. The question of how far the specific heats of magnetic transitions can be represented by the logarithmic form was discussed by T. Yamamoto (Kyoto University). The discussions indicated that, although the specific heat of several gases and many magnetic systems can be represented by the same logarithmic function which represents the specific heat near the λ-point of liquid helium over several decades of T-T_c, in none of these transitions was the logarithmic singularity confirmed as unequivocally as for the helium λ-point. It was pointed out by Fisher that the experiments of Voronel *et al.* and Moldover and Little could be represented by a small positive power of $|T$-$T_c|$. This would be more in agreement with the results of the series summation methods and with the conclusions drawn from the inequalities derived by Rushbrooke and Griffiths. Following discussions by M. H. Edwards (Stanford University) on the coexistence curve of liquid helium, and by H. Kierstead (Argonne National Laboratory) on a logarithmic anomaly, the pressure coefficient, in another property of helium close to the λ-line, M. J. Buckingham presented his theory on the nature of cooperative transition. This theory proceeds in quite a different direction from others.

The quantity of light scattered in a given direction at a given wavelength by the fluctuations of an opalescent medium is related by a very simple Fourier transformation to the pair correlation function of the fluctuations. The intensity of inelastically scattered light, which depends on both the frequency and the wave vector, is related by a somewhat more general Fourier transform formula to the temporal sequence of the density fluctuations. In the absence of Elliott Montroll (Institute for Defense Analyses), who was to have discussed the theoretical provenance of this relationship as well as of its limitations, Debye (Cornell University) commented on this topic. He warned that the very convenient Fourier transform formulas are based on the Born approximation theory of scattering. In a region of large fluctuation, one must be concerned with nonlinear effects not given by the Born approximation. With this *caveat* in mind, Michael Fisher (King's College, London) reviewed the statistical mechanical theory of the pair correlation function. Fisher pointed out that the essential assumption of the Ornstein-Zernike theory is that the "direct correlation function" is short-range even at the critical point. This seemingly innocuous assumption immediately leads to the conclusion that the correlation function itself is long-range and behaves like $1/R$ for large distances. The fact that light scattering experiments are in very good agreement with the Ornstein-Zernike theory, except very close to the critical point, indicates that this is quite a good assumption. Several authors, however, have suggested that the direct correlation function is probably not short-range at the critical point, and in fact this assumption is inconsistent with the rigorous pair correlation function derived by Onsager for the two-dimensional Ising model. Fisher's own investigation with the series summation method suggests that the pair correlation function decays like $1/R$ to a power slightly less than 1.

The present experimental status of light and x-ray scattering from critically opalescent systems was discussed in a review by H. Brumberger (Syracuse University). Critical scattering has often been studied, but only a few of the most recent experiments have been done carefully enough to test the Ornstein-Zernike theory. B. Chu (University of Kansas) briefly reviewed his careful experiments on the scattering of light from a number of binary liquid mixtures. These experiments beautifully confirmed earlier results of McIntyre and others that large and significant deviations from the Ornstein-Zernike theory become manifest for temperatures of the order of hundredths of a degree from the critical point.

One of the most interesting questions before the conference was the apparent contradiction between the experimental results of L. Passel (Brookhaven) and B. Jacrot (Saclay) on critical magnetic scattering of neutrons from iron and the theory of Van Hove. Both experimenters observed a finite inelasticity of the scattering even at the critical point, while the theory of Van Hove, just as unequivocally, showed that the scattering must be inelastic at the critical point. Marshall resolved this contradiction by postulating the persistence of spin waves, much altered by dissipative effects, even up to the critical point. After Passel commented on the work by Marshall and by Als-Neilsen and Deitrich of RISO, Denmark, on elastic neutron scattering from β-brass, the interesting question of the inelastic scattering of light from criti-



cally opalescent systems was raised. The observation of this effect has only recently become possible because of the existence of lasers. Two groups of investigators have recently succeeded in observing this effect. The effect was first observed by Alpert and Yeh (Columbia University) in a critically opalescent mixture of cyclohexane and aniline, and shortly after by Ford and Benedek (M.I.T.). There is much uncertainty in the experimental results on equilibrium critical phenomena and there is even more in the observation of nonequilibrium critical phenomena. J. Sengers (National Bureau of Standards) reviewed experimental work on transport properties of liquids, gases, and liquid mixtures near critical points. Perhaps the most surprising conclusion was the fact that viscosity exhibits no observable anomaly near the critical point of gases, whereas thermal conductivity exhibits a very large and possibly infinite value near the critical point. The reasons for this were the subject of an interesting but inconclusive discussion following Sengers' talk. After a short presentation on nuclear magnetic resonance experiments near the critical point of ethane by M. Bloom (Harvard University and the University of British Columbia) the question of ultrasonic propagation in the neighborhood of critical points was raised. C. E. Chase (M.I.T.) discussed the ultrasonic investigation of helium near its critical points, and C. Garland (M.I.T.) spoke on the ultrasonic investigation of ammonium chloride near its order-disorder transition.

The rather concentrated work of the conference was interrupted by an evening of socializing and relaxation at a banquet. Philip H. Abelson (editor of *Science* and director of the Carnegie Institution Geophysical Laboratory) spoke on the role of group interaction in scientific research.

The emphasis of the conference was mainly on experiment, reflecting the present situation in the field. The significance of much experimental data is being sorted out. The older theories give the broad outlines of the phenomena but are incapable of explaining the delicate behavior in the immediate neighborhood of the critical point.

The conference proceedings will appear in the National Bureau of Standards Miscellaneous Publications series and will be available through the Government Printing Office. Inquiries about the proceedings should be directed to the undersigned.

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M. S. GREEN
National Bureau of Standards, Washington, D.C.

Forthcoming Events

October

15–17. **Growth**, intermountain regional conf., Alta, Utah. (E. W. Hanly, Dept. of Molecular and Genetic Biology, Univ. of Utah, Salt Lake City)

16–17. **Infectious Diseases** Soc. of America, Washington, D.C. (E. H. Kass, IDS, Boston City Hospital, Boston, Mass.)

17–21. **Antimicrobial Agents and Chemotherapy**, 5th interscience conf./4th intern. congr. of chemotherapy, Washington, D.C. (R. W. Sarber, American Soc. for Microbiology, 115 Huron View Blvd., Ann Arbor, Mich.)

17–21. **Metallurgical** Soc. of American Inst. of Mining, Metallurgical, and Petroleum Engineers, Detroit, Mich. (American Inst. of Mechanical Engineers, 345 E. 47 St., New York 10017)

18. **Industrial Pharmacy** sect., American Pharmaceutical Assoc., 4th annual midwest regional meeting, Chicago, Ill. (C. Schroeter, Abbott Laboratories, North Chicago, Ill.)

18–19. American Inst. of **Aeronautics and Astronautics**/Canadian Aeronautics and Space Inst., Toronto, Ont., Canada. (D. L. Raymond, 1290 Sixth Ave., New York 10019)

18–19. **Systems Science**, conf., Case Inst. of Technology, Cleveland, Ohio. (Inst. of Electrical and Electronics Engineers, Box A, Lenox Hill Station, New York 10021)

18–20. **Dynamic Stability of Structures**, intern. conf., Evanston, Ill. (G. Herrmann, Technological Inst., Northwestern Univ., Evanston 60201)

18–20. **Electromagnetic Radiation in Agriculture,** intern. conf., Roanoke, Va. (D. P. Brown, Niagara Mohawk Power Corp., 300 Erie Blvd. W., Syracuse, N.Y. 13212)

18–20. American Soc. of **Lubrication Engineers**, San Francisco, Calif. (D. B. Sanberg, 5 North Wabash Ave., Chicago, Ill.)

18–20. Canadian Inst. of **Mining and Metallurgy**, annual western meeting, Winnipeg, Canada. (CIMM, 906 Drummond Bldg., 1117 St. Catherine St. W., Montreal 2, P.Q., Canada)

18–20. **Nuclear Science**, 12th symp., San Francisco, Calif. (Inst. of Electrical and Electronics Engineers, Box A, Lenox Hill Station, New York 10021)

18–20. Applied **Spectroscopy**, 12th symp., Ottawa, Ont., Canada. (R. V. Baker, Aluminum Co. of Canada, Arvida, P.Q., Canada)

18–21. Advances in **Gas Chromatography**, 3rd intern. symp., Houston, Tex. (A. Zlatkis, Dept. of Chemistry, Univ. of Houston, Houston)