

Reprinted from: QUANTUM FLUIDS AND SOLIDS (1977)

Edited by Samuel B. Trickey, E. Dwight Adams, and James W. Dufty

Book available from: Plenum Publishing Corporation

227 West 17th Street, New York, N.Y. 10011

OPTICAL EXPERIMENTS IN ^3He - ^4He MIXTURES NEAR THE TRICRITICAL POINT

P. Leiderer

Physik-Department E 10 der Technischen Universität München
8046 Garching, West Germany

In the vicinity of a critical point, a number of important properties can be determined by means of optical methods.¹ As an example let us consider a binary mixture near its consolute critical point where the observed "critical opalescence" is due to the increasing fluctuations in concentration.

From the intensity of the light scattered from these fluctuations the concentration susceptibility with its critical exponent γ can be obtained. The wave vector dependence of the scattered light provides insight into the size of the concentration fluctuations, *i.e.*, the correlation length ξ , with its critical exponent ν . Spectral resolution of the scattered light shows the time scale of the concentration fluctuations, and in general a "critical slowing down" of these fluctuations is observed on approaching the critical point. The order parameter, which for a binary mixture is the concentration difference between the two coexisting phases, can also, among other methods, be determined optically by measuring the difference in the index of refraction. Finally, the interfacial tension in the phase separated mixture can be obtained using light scattering from interfacial waves.

In principle, helium is not an ideal candidate for light scattering experiments because its polarizability is quite small and therefore the scattered light intensities are very weak. Nevertheless, all the properties mentioned above have been measured in ^3He - ^4He mixtures near the tricritical point (temperature $T_t \approx 0.867\text{K}$, ^3He -concentration $x_t \approx 0.6752$) demonstrating that even in this case optical methods can serve as a versatile tool in determining critical exponents.

The experimental set-up for all the measurements described here was essentially the same, with some modifications according to the particular quantity to be measured. It is shown schematically in Fig. 1. Because of the low light levels, a photon counting technique with the appropriate analyzing equipment was used for detection of the scattered intensities. In the following the main results of these measurements are described.

ORDER PARAMETER

Of the two order parameters near the tricritical point - the superfluid order parameter and the order parameter of the non-ordering density, which is the concentration difference $\Delta x = x_+ - x_-$ between the coexisting normal and superfluid phases - only the latter is easily accessible optically. The limiting angle of total reflectivity of the interface in the phase separated mixture yields directly the discontinuity of the refractive index, $\Delta n = n_- - n_+$, across the interface, and by means of the relation $\partial n / \partial x = 0.0070^3$ the concentration difference Δx is obtained. This method determines the order parameter free of gravity perturbations, since only the interface itself is involved in the measurement, and in addition provides calibration for temperature differences from T_t to better than 0.1mK.

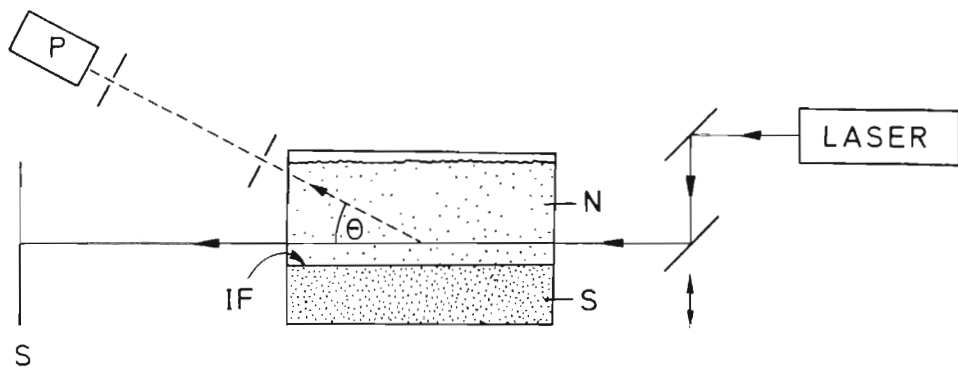


Figure 1. Schematic set-up for optical experiments in ^3He - ^4He mixtures. When the laser beam is scanned vertically across the sample cell, the photomultiplier P registers the light scattered at an angle θ from the upper normal (N) or lower superfluid (S) phase, respectively. When the laser beam traverses the cell exactly at the position of the interface IF, an additional spot appears on the screen S due to diffraction of part of the incident light at the limiting angle of total reflectivity.

Δn is found to decrease linearly on approaching T_t , as shown in Fig. 2, implying $\Delta n \propto t^\beta$ ($t = T_t - T/T_t$), where the tricritical exponent is $\beta=1.0$ in the range $8 \times 10^{-4} < t < 10^{-2}$. This result confirms that the phase separation curve in ^3He - ^4He mixtures, as opposed to conventional binary mixtures, has an angular top, as first observed by Graf *et al.*⁴ This already indicates that ^3He - ^4He mixtures near the tricritical point belong to a universality class different from that of simple fluids and conventional binary mixtures, with completely different, mean-field-like critical exponents.^{5,6}

CONCENTRATION SUSCEPTIBILITY AND CORRELATION LENGTH

Light scattering intensities give a direct measure of the concentration susceptibility $(\partial x / \partial \Delta)_{T,p}$ near T_t in the small scattering vector limit ($q \rightarrow 0$), in contrast to experiments on specific heat⁷ and saturated vapor pressure.⁸ In the hydrodynamic regime, $q\xi \ll 1$, the scattering power is proportional to the extinction length

$$h = A(\lambda) \frac{k_B T}{v} \left[\frac{1}{v} \left(\frac{\partial v}{\partial x} \right)_{TP}^2 \left(\frac{\partial x}{\partial \Delta} \right)_{TP} + \beta_{Tx} \right] \quad (1)$$

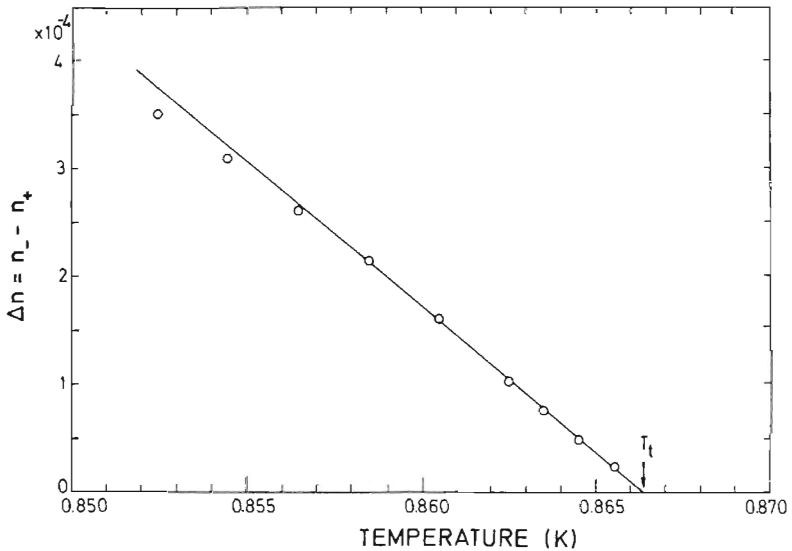


Figure 2. Discontinuity of the index of refraction, n , across the interface of the phase separated mixture, as determined from the limiting angle of total reflectivity. The accuracy of the absolute temperature scale is $\pm 1\text{mK}$ due to uncertainties in the ^3He vapor pressure calibration. Error bars for Δn are smaller than the size of the data symbols.

where $A(\lambda) = (2\pi/\lambda)^4 (4\pi\alpha N_0)^2/6\pi$ and $\beta_{TX} = -(1/v) (\partial v/\partial p)_{TX}$.

Here $\Delta = \mu_3 - \mu_4$ is the difference between the chemical potentials of ^3He and ^4He , v is the molar volume, αN_0 is the molar polarizability of helium, and λ is the light wavelength. The isothermal compressibility β_{TX} varies only weakly near the tricritical point, whereas the concentration susceptibility is expected to diverge. Since the atomic volumes of ^3He and ^4He differ, concentration fluctuations dominate the scattering and the critical opalescence is determined by the divergence of $(\partial x/\partial \Delta)_{TP}$.⁹

To keep gravitational effects on light scattering to a minimum while very close to T_t , the incident laser beam was focused and scanned vertically across the sample cell. In this way the scattered intensity was monitored <0.2 mm away from the interface, thus providing data essentially free of gravity effects when $T_t - T > 0.002\text{K}$. Apparent concentration susceptibility data $(\partial x/\partial \Delta)_{TP}$, shown in Fig. 3, were obtained from the scattered intensities by using Eq. (1), i.e. by heuristically assuming isotropic scattering for the $q \rightarrow 0$ limit. The results were fitted by the expected power-law divergence of the form $(\partial x/\partial \Delta)_{TP} = G \cdot t^{-\gamma}$.

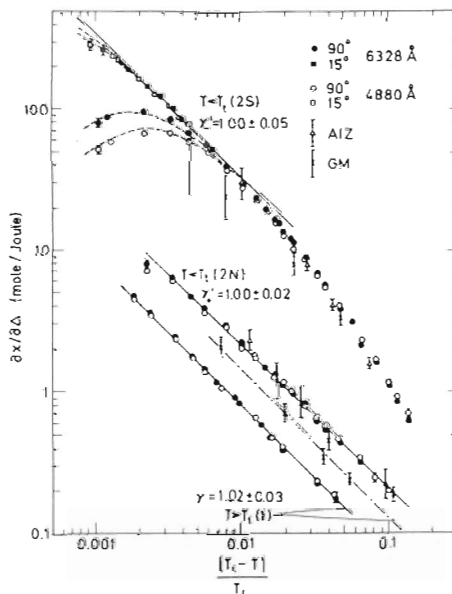


Figure 3. Log plot of $(\partial x/\partial \Delta)_{TP}$ vs. t for the single phase (1), and for the coexisting normal (2N) and superfluid (2S) phases for a mixture with $x=0.6749$. For comparison, data of Alvesalo *et al.* (AIZ) and Goellner and Meyer (GM) (Refs. 7 and 8) are shown. The dashed lines show the best fit to our data calculated according to Eq. (2). At $t \lesssim 10^{-3}$, the remaining small discrepancy is attributable to gravity effects.

For the single phase critical isochore and the normal coexisting phase, power laws were found to hold in the entire investigated temperature interval. In contrast, the tricritical region for the superfluid seems to be confined to $T_t - T < 10\text{mK}$, about the same temperature interval in which the phase diagram is linear (c.f. Fig. 2). The best-fit critical exponents are $\gamma = 1.02 \pm 0.03$, $\gamma_+ = 1.00 \pm 0.02$, and $\gamma_- = 1.00 \pm 0.05$, where γ applies for $T < T_t$ along the critical isochore and γ_+ and γ_- for $T < T_t$, the subscripts + and - referring to the normal and superfluid coexisting phases, respectively.

To obtain the correlation length ξ of the concentration fluctuations, the wave number dependence of the scattered intensity was determined by using two wavelengths, $\lambda = 6328\text{\AA}$ and 4880\AA , and two scattering angles, 90° and 15° , thus providing data at four wave numbers. The onset of q -dependence of the 90° scattering intensities in the coexisting superfluid is clearly evident in Fig. 3 for $t < 0.007$. A comparison with the modified Ornstein-Zernicke expression for the correlation function calculated by Furman and Blume¹⁰ shows that the data can be well represented by the correlation function

$$C(\vec{q}, t) \approx \frac{\text{const.}}{q} \left(\frac{q/t}{1.6 \times 10^{-16} q^2/t^2 + 1} \right) \quad (2)$$

If we define the critical exponents η and ν by writing $C(\vec{q}, t) = 1/q^{2-\eta} F(q/t^\nu)$, we find that the experimental results are consistent with the critical exponents $\nu = 1$ and $\eta = 1$. Thus the correlation length in the superfluid phase is given by $\xi = 1.3 t \text{ \AA}$. Note that in the normal phases a much smaller, if any, deviation from the straight lines in Fig. 3 suggests a considerably smaller correlation length there - another indication of the large asymmetry in the amplitude of the power laws near T_t , as obvious already from the magnitudes of the concentration susceptibility in Fig. 3, and also from the different slopes of the phase separation curves.²

TRICRITICAL SLOWING DOWN

Similar to the correlation length, the relaxation time of the fluctuations also increases near a critical point. This is reflected in the spectrum of the scattered light as a narrowing of the central Rayleigh line (which is the one dominated by the scattering from concentration fluctuations) to typically less than 10^3 Hz. For a spectral analysis this requires resolutions $\Delta\nu/\nu < 10^{-13}$, nowadays attained by light beating spectroscopy. However, for this technique relatively high light intensities are

necessary, and in $^3\text{He}-^4\text{He}$ mixtures only the superfluid phase has so far been accessible to measurement;¹¹ in the normal phase where the concentration susceptibility and consequently the scattering power is an order of magnitude smaller than in the superfluid phase, the light intensities were too small for such an analysis.

The resulting reduced Rayleigh linewidth Γ/q^2 for scattering at $\theta=15^\circ$ is plotted in Fig. 4 for laser wavelengths $\lambda=4880$ and 6328\AA , corresponding to scattering vectors $q=3.35 \times 10^4$ and $2.59 \times 10^4 \text{ cm}^{-1}$, respectively. The reduced linewidth is used because by comparison with Fig. 3 the data are expected to lie in the hydrodynamic regime, where the linewidth generally is given by $\Gamma=D_{\text{eff}} \cdot q^2$ with an effective diffusion coefficient D_{eff} . Indeed in this representation the data for different q collapse to a single line

$$\frac{\Gamma}{q^2} = D_{\text{eff}} = 1.5 \times 10^{-4} \cdot t^{0.95 \pm 0.07} \text{ cm}^2/\text{sec} \quad (3)$$

Siggia and Nelson¹² have treated the problem of fluctuation lifetimes theoretically by means of renormalization group methods. In the hydrodynamic regime they predict the existence of two diffusive modes: one with eigen-frequency $\omega_1 \propto t q^2$, which seems to be observed here, and one with $\omega_2 \propto t^{-2/3} q^2$ which has been detected very recently in sound attenuation measurements.¹³

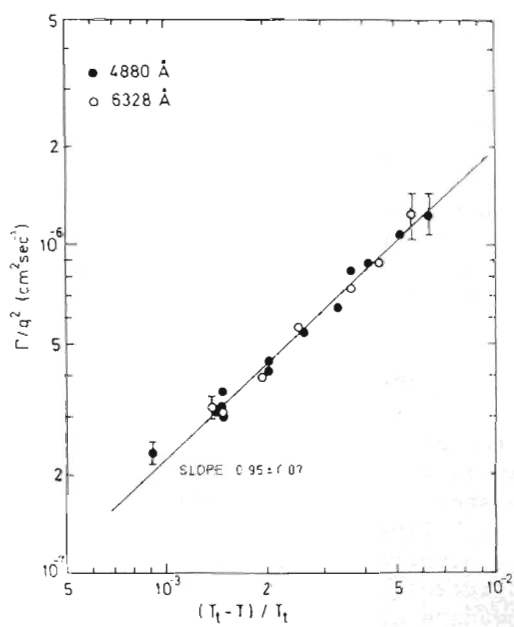


Figure 4. Reduced Rayleigh linewidths at 15° scattering angle.

LIGHT SCATTERING FROM THE INTERFACE

One can now use the above results for the critical exponents to predict the behavior of other properties near the tricritical point. One such property is the interfacial tension.

As a phase separated binary mixture approaches its critical point and the two phases become more and more similar, the interfacial tension - which is the free energy associated with unit interface area - vanishes as¹⁴

$$\sigma_i \propto (T_c - T)^\mu \quad (4)$$

Up to now no rigorous theory exists which links the interfacial tension to properties of the bulk system. However, a phenomenological approach which should be valid in the vicinity of the critical point has been developed by Fisk and Widom,¹⁵ who obtain for the interfacial tension

$$\sigma_i = c \cdot \frac{L}{\chi} \cdot (\Delta x)^2 \quad (5)$$

where L is the thickness of the interface, χ the concentration susceptibility, Δx the concentration difference of the two phases, and c some numerical constant of the order $1/6$, the exact value depending on the detailed shape of the interfacial profile. The interfacial thickness is generally assumed to be of the order of the bulk correlation length ξ . Hence (5) implies the scaling relation¹⁵

$$\mu = \gamma' - \nu' + 2 \quad (6)$$

At the consolute critical point of a binary mixture like cyclohexane-methanol Eq. (6) yields $\mu \approx 1.28$, in good agreement with experiment.¹⁶ At the tricritical point of $^3\text{He}-^4\text{He}$, with the exponents given as discussed above, the prediction from scaling is $\mu=2$, as pointed out by Papoular.¹⁷

One way to check this prediction and to determine the interfacial tension experimentally is to study interfacial waves. If we neglect damping for the moment, the dispersion relation of interfacial waves (ripples) is given by

$$\omega^2 = \frac{\rho_- - \rho_+}{\rho_- + \rho_+} gk + \frac{\sigma_i}{\rho_- + \rho_+} k^3 \quad (7)$$

where the restoring force in the first contribution is supplied by gravity and in the second term by the interfacial tension. Here ω and k are the angular frequency and wave number of the ripplon, ρ_+ and ρ_- the density of the ^3He -rich and ^4He -rich phase, respectively, and g the acceleration of gravity.

In our experiment, the interfacial waves were generated artificially by a coil of bifilar wires (cf. inset in Fig. 5), to which an a.c. voltage was applied, a set-up similar to that of Boldarev and Peshkov.¹⁸ For the detection of the waves, the incident laser beam was reflected from the interface at a small angle. The interfacial waves act like a phase grating on the reflected beam and give rise to a Debye-Sears-like pattern of interference fringes, the fringe distance yielding the wavelength of the interfacial waves.

Knowing the wavelength and frequency of the ripplons, the interfacial tension can be obtained from the dispersion relation (7).¹⁹ The resulting interfacial tension is plotted in Fig. 5. In the whole temperature range investigated, $20\text{mK} < T - T_c < 370\text{mK}$, σ_i can be represented by

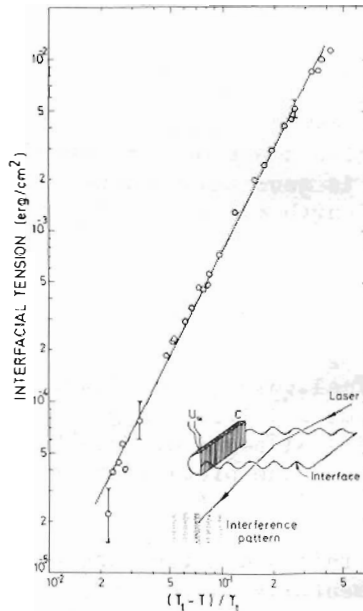


Figure 5. Interfacial tension of phase separated ^3He - ^4He mixtures, calculated from the dispersion of interfacial waves. Damping of the waves has been taken into account.¹⁹ The straight line is a fit according to Eq. (8). In the inset, the scattering geometry is shown. The interfacial waves are generated with the bifilar coil C.

$$\sigma_i = \sigma_{i0} t^\mu \quad (8)$$

where $\sigma_{i0} = 0.076 \text{ erg/cm}^2$, and $\mu = 2.0$, as expected from scaling.¹⁷ This is a much stronger variation with temperature than observed near conventional critical points, where $\mu = 1.28$, and indicates the influence of the tricritical point.

In most critical systems studied previously the borderline dimensionality where mean field theory should apply²⁰ is $d=4$ and is hence not accessible experimentally. From the experiments described here, a nearly complete set of critical exponents has been obtained for the first time for a system with borderline-dimensionality²¹ $d=3$, where the critical exponents are mean-field-like. These exponents $\beta = \gamma_{\pm}^{\prime} = \nu^{\prime} = \eta^{\prime} = 1$, $\mu = 2$ are consistent with scaling, e.g. $\gamma = (2 - \eta) \cdot \nu$, $\mu = \gamma - \nu + 2\beta$, etc. Much more accurate measurements are necessary to determine any logarithmic corrections to these pure power law dependences, as predicted by renormalization group theory.^{21,22}

ACKNOWLEDGEMENTS

The work reported here was done in collaboration with W. W. Webb, D. R. Watts, D. R. Nelson, M. Wanner, and H. Poisel. Thanks are due to P. C. Hohenberg, B. Widom, M. Papoular and H. Kinder for many valuable discussions. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

- (1) For a review, see P. Heller, Rep. Progr. Phys. 30, 731 (1967).
- (2) See for example G. Ahlers, in "The Physics of Liquid and Solid Helium," edited by K. D. Bennemann and J. B. Ketterson (Wiley, New York, 1976), Part I.
- (3) H. A. Kierstead, J. Low Temp. Phys. 24, 497 (1976).
- (4) E. H. Graf, D. M. Lee, and J. D. Reppy, Phys. Rev. Lett. 19, 417 (1967).
- (5) R. B. Griffiths, Phys. Rev. Lett. 24, 715 (1970), and Phys. Rev. B7, 545 (1973), and references cited therein.
- (6) E. K. Riedel, Phys. Rev. Lett. 28, 675 (1972).

- (7) T. Alvesalo, P. Berglund, S. Islander, G. R. Pickett, and W. Zimmermann, Jr., Phys. Rev. Lett. 22, 1281 (1969), and Phys. Rev. A 4, 2354 (1971).
- (8) G. Goellner and H. Meyer, Phys. Rev. Lett. 26, 1534 (1971); G. Goellner, R. Behringer, and H. Meyer, J. Low Temp. Phys. 13, 113 (1973).
- (9) P. Leiderer, D. R. Watts, and W. W. Webb, Phys. Rev. Lett. 33, 483 (1974).
- (10) D. Furman and M. Blume, Phys. Rev. B 10, 2068 (1974).
- (11) P. Leiderer, D. R. Nelson, D. R. Watts, and W. W. Webb, Phys. Rev. Lett. 34, 1080 (1975).
- (12) E. D. Siggia and D. R. Nelson, to be published.
- (13) D. B. Roe, G. Ruppeiner, and J. Meyer, to be published.
- (14) For a review, see B. Widom, in "Phase Transitions and Critical Phenomena," edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2, Chap. III.
- (15) S. Fisk and B. Widom, J. Chem. Phys. 50, 3219 (1969).
- (16) C. Warren and W. W. Webb, J. Chem. Phys. 50, 3694 (1969).
- (17) M. Papoular, Phys. Fluids 17, 1038 (1974).
- (18) S. T. Boldarev and V. P. Peshkov, JETP Lett. 17, 297 (1973).
- (19) For a more detailed analysis, the damping of the interfacial waves has to be taken into account. See M. A. Bouchiat and J. Meunier, J. Phys. (Paris) 32, 561 (1971); J. Phys. (Paris) 33, C1-141 (1972); E. S. Wu and W. W. Webb, Phys. Rev. A8, 2077 (1973); P. Leiderer, H. Poisel, and M. Wanner, to be published.
- (20) See, for example, B. Widom in "Fundamental Problems in Statistical Mechanics," Vol. 3, Edited by E. D. G. Cohen (North-Holland Publishing Company, Amsterdam, 1975).
- (21) E. K. Riedel and F. J. Wegner, Phys. Rev. Lett. 29, 349 (1972).
- (22) M. J. Stephen, E. Abrahams, and J. P. Straley, Phys. Rev. B 12, 256 (1975).