Interfacial Tension Near the Tricritical Point in ^3He - ^4He Mixtures

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The interfacial tension σ_i of phase-separated ^3He - ^4He mixtures has been measured between 0.5 K and the tricritical point. The observed decrease of σ_i on approaching the tricritical point is much stronger than for ordinary critical points. Our data are consistent with a critical exponent $\mu = 2$.

As a liquid-vapor system approaches its critical point and the two phases become more and more similar, the interfacial tension σ —which is the free energy associated with unit interface area—vanishes. Sufficiently close to the critical point, σ is described by a power law with a critical exponent μ (see Ref. 1 for a review):

$$\sigma \propto (T_c - T)^\mu \quad (1)$$

The same relationship holds for the interfacial tension σ_i at the consolute critical point (the critical point for phase separation) of a binary fluid mixture.

Up to now no rigorous theory 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.² According to their theory, the interfacial tension for a binary mixture is given by

$$\sigma_i = c(L/\chi)(\Delta x)^2 \quad (2)$$

where L is the thickness of the interface, χ is the concentration susceptibility, Δx is the concentration difference of the two phases, and c is 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. With ν' , γ' , and β

the critical exponents of L , χ , and Δx , Eq. (2) implies the scaling relation

$$\mu = \gamma' - \nu' + 2\beta \quad (3)$$

In experiments near the consolute critical point of a binary mixture like cyclohexane-methanol, reasonable agreement with these predictions was observed: Warren and Webb³ measured a value of $\mu = 1.23 \pm 0.05$, as compared to $\mu \approx 1.28$ expected from Eq. (3); the magnitude of σ_i calculated from (2) was found to agree with experiment within a factor of two.

In ^3He - ^4He mixtures near the tricritical point (temperature $T_t \approx 0.867$ K, ^3He concentration $X_t \approx 0.675$), mean-field-like exponents determine the behavior of the system.^{4,5} The exponents $\gamma' \sim 1$ and $\beta \sim 1$ have been determined in a number of experiments,⁶⁻⁹ whereas the correlation length, and hence the exponent ν' , has only been determined for the superfluid phase from light scattering data, with the result $\nu' \sim 1$.⁹ With this set of exponents the interfacial tension is expected to vanish near T_t with a critical exponent $\mu = 2$, as pointed out by Papoular.¹⁰

We have obtained the interfacial tension of phase-separated ^3He - ^4He mixtures from an interfacial wave experiment. If we neglect damping for the moment, the dispersion relation of interfacial waves (ripples) is given by¹¹

$$\omega^2 = \frac{\rho_- - \rho_+}{\rho_- + \rho_+} gq + \frac{\sigma_i}{\rho_- + \rho_+} q^3 \quad (4)$$

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

The interfacial waves were generated by a coil of bifilar wires (cf. inset in Fig. 1), a setup similar to that of Boldarev and Peshkov.¹² The power dissipation of such an array is very small ($< 10^{-9}$ W) as compared to other methods,^{13,14} which makes it well suited for investigations in the vicinity of a critical point. When an ac voltage U with frequency f_{ac} is applied to the electrodes formed by the two separately insulated wires, the interface is pulled up periodically. The corresponding force acting on the interface is expected to vary like U^2 ; hence the frequency of the interfacial waves generated in this way should be $f_i = 2f_{ac}$. Our measurements, however, show quite unequivocally an elongation of the interface proportional to U and a frequency of the generated waves equal to f_{ac} . This might indicate the presence of additional charges in our sample chamber; a more clear-cut explanation is lacking at present.

For the detection of the interfacial waves, the attenuated beam (10^{-4} W) of a He-Ne-laser was reflected from the interface at a small angle.

The waves act like a phase grating on the reflected beam and give rise to a Debye-Sears-like¹⁵ pattern of interference fringes, the fringe distance yielding the wavelength of the interfacial waves.

Knowing the wavelengths corresponding to several frequencies at constant temperature, one can in principle obtain σ_i and $\Delta\rho = \rho_- - \rho_+$ from a fit to the dispersion relation of Eq. (4).^{*} We preferred, however, to determine $\Delta\rho$ independently by measuring the limiting angle of total reflection at the interface, which gives the ratio of the refractive indices of the ^3He - and ^4He -rich phases. By means of the Clausius-Mosotti relation and the known molar volumes,¹⁶ $\Delta\rho$ can then be calculated quite accurately. Since in the vicinity of the tricritical point $\Delta\rho \propto T_i - T$, this method allows in addition a precise and independent evaluation of the tricritical temperature T_i .⁹ We found $T_i = 0.867 \pm 0.001$ K, the error being mainly due to uncertainties of the ^3He vapor pressure calibration.

In Fig. 1. the angular frequency of the interfacial waves is plotted versus wave number q for the temperature $T_i - T = 72$ mK. At large wave numbers the "capillary contribution" in the dispersion relation (4) dominates and leads to an $\omega \propto q^{3/2}$ behavior. The changing slope at small q is mostly due to the growing influence of the gravity term in (4).

In experiments at liquid-vapor interfaces Bouchiat and Meunier¹⁷ and Wu and Webb¹⁸ observed that for a detailed analysis of their data they had to take the damping of the interfacial waves into account. Then the simple relation (4) has to be modified and is implicitly given by[†]

$$y = \frac{-2\rho_- \rho_+}{(\rho_- + \rho_+)^2} S(1 + 2S)_{(+)}^{1/2} [1 + (1 + 2S)_{(+)}^{1/2}] - \left(\frac{\rho_- - \rho_+}{\rho_- + \rho_+} \right)^2 [(1 + S)^2 - (1 + 2S)_{(+)}^{1/2}] \quad (5)$$

where $S = S_r \pm iS_i = \tau_0 [(-1/\tau) \pm i\omega]$, τ is the lifetime of the wave, $(\dots)_{(+)}^{1/2}$ means the square root has a positive real part, and τ_0 and y are defined as

$$\tau_0 = (\rho_+ + \rho_-)/2(\eta_+ + \eta_-)q^2$$

$$y = \{[(\rho_- - \rho_+)g + \sigma_i q^2]/4q^3\}[(\rho_- + \rho_+)/(\eta_- + \eta_+)^2] \quad (6)$$

^{*}In the investigated temperature range, $0.5 \text{ K} < T < T_i$, the sum of the densities $\rho_+ + \rho_-$ can be considered to be nearly constant.

[†]In this approximation, retardation effects of the bulk flows are neglected. We have used Eq. (5) in this preliminary analysis to avoid the mathematical complications involved in solving the exact relation (see Ref. 18). Within our experimental accuracy we cannot distinguish between the exact form and (5).

Fig. 1. Dispersion of interfacial waves in a phase-separated ^3He - ^4He mixture. Circles show the experimental values, while the solid line reflects the theoretical dependence according to Eq. (5), including the measured damping of the waves. The insert schematically shows the experimental array.

Equation (5) contains as an additional parameter $\eta_+ + \eta_-$, the sum of the viscosities of the ^3He - and ^4He -rich phases. To be able to determine the damping and hence $\eta_+ + \eta_-$ experimentally, we used a detection technique different from the interference method described above. The incident laser beam was focused at the interface to a diameter much smaller than the interfacial wavelength, and was therefore slightly deflected periodically by the propagating wave. The *amplitude* of this angular modulation is directly connected with the wave amplitude at the focal volume, whereas the *phase* of the modulated signal is equal to the phase of the interfacial wave at that point. Therefore, shifting the focal volume away from the wave generator allows a measurement of both wavelength and attenuation.

When damping is taken into account in this way, our experimental data are well represented by the dispersion relation (5), as is indicated in Fig. 1. The only parameter in fitting the solid curve is the interfacial tension σ_i , which for this temperature was evaluated as $4.73 \times 10^{-4} \text{ erg/cm}^2$. The dynamics of the ^3He - ^4He interface is obviously well described by the

classical dispersion relation, although here the interface is a boundary between a superfluid and a normal quantum liquid. On the other hand, this might not be too surprising, because the classical relation was also found to hold at the surface of pure ^4He .^{13,14,19,20} The sum of the viscosities $\eta_+ + \eta_-$ at $T_t - T = 72$ mK as determined from the attenuation is $40 \pm 5 \mu\text{P}$, in good agreement with the value $38 \mu\text{P}$ found by Lai and Kitchens²¹ with a vibrating wire viscosimeter. An amplitude dependence was observed neither for the damping nor for the wavelength λ when the amplitude a of the interfacial wave was varied at fixed frequency by two orders of magnitude in the range $10^{-4} < a/\lambda < 10^{-2}$; therefore we believe that the measurements are not disturbed by nonlinear effects.

With the described method the interfacial tension was determined for temperatures $20 < T_t - T < 370$ mK. As is displayed in Fig. 2, in this interval σ_i decreases rapidly by three orders of magnitude on approaching the

Fig. 2. Interfacial tension σ_i of a ^3He - ^4He mixture ($x = 0.675$) at saturated vapor pressure versus temperature difference $\Delta T = T_t - T$. The straight line indicates a slope of two.

tricritical point. Close to T_t the value for σ_i is, to our knowledge, the smallest observed for an interfacial or a surface tension so far (and is about 10^{-6} of the surface tension of water at room temperature). A comparison with existing data far away from T_t shows good agreement with the result of Guo *et al.*,²² $\sigma_i = 0.011 \pm 0.003$ erg/cm² at 0.515 K, and also with the measurement of Boldarev and Peshkov,¹² whereas the values for σ_i quoted by Dickson *et al.*²³ differ from ours by one order of magnitude.

In the whole temperature range investigated $\sigma_i(T)$ can be represented by

$$\sigma_i = \sigma_0 t^\mu, \quad 2.3 \times 10^{-2} < t < 4.3 \times 10^{-1} \quad (7)$$

where $\mu = 2.0 \pm 0.12$, $\sigma_0 = 0.076$ erg/cm², and $t = 1 - (T/T_t)$.

This is a much stronger variation with temperature than observed near conventional critical points, where $\mu \sim 1.28$,¹ and indicates the influence of the tricritical point. The value of μ is consistent with the expectation from scaling, $\mu = 2$.¹⁰

The apparent wide range of the tricritical region for σ_i is unexpected, since the properties of the interface should be determined by both the superfluid and the normal phases. The latter has a relatively wide critical regime of $t \lesssim 10^{-1}$, where the expected asymptotic power laws hold. However, in the superfluid phase that regime is known to extend only to $t \lesssim 10^{-2}$.⁹ Therefore we consider the exponent μ in our measurement as an effective exponent, which might depend partly on cancellations in the temperature dependences of bulk properties like the coherence length and the concentration susceptibility. Measurements closer to the tricritical point have yet to demonstrate whether μ as determined here has already reached its asymptotic value.

For binary mixtures, where the properties of the two coexisting phases are symmetric with respect to the critical point, the numerical value of σ_i can be estimated by means of Eq. (2). An extended theory is necessary, however, for ³He–⁴He mixtures, because these are highly asymmetric: The amplitudes of the concentration ($x - x_c$) for the ³He-rich and ⁴He-rich branches of the phase diagram differ by a factor of five, the amplitudes of the concentration susceptibility by a factor of ten, and a similar situation seems to exist for the correlation length. Regarding these asymmetries, it cannot be excluded that one of the two coexisting phases dominates the behavior of the interfacial tension near the tricritical point.

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