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Thermodynamic Properties of Liquid He^3/He^4 Mixtures Near the Tricritical
Point Derived from Specific Heat Measurements

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In a recent publication we presented the results of some measurements of the specific heat of liquid He^3/He^4 mixtures at saturated vapor pressure near the interesting junction of the lambda and phase-separation curves which occurs at a temperature $T_0 \approx 0.87^\circ\text{K}$ and a He^3 mole fraction $x_0 \approx 0.67$.¹ The purpose of the present report is to indicate some of the possibilities for determining a variety of thermodynamic information about the junction region from the specific heat data.²

The junction is a point at which a first-order phase transition goes over into a second-order transition with increasing temperature. Griffiths has argued that when the additional thermodynamic dimension associated with the superfluid order parameter and its conjugate field is included, the junction point represents the intersection of three critical lines, the λ -curve and two new ones, and has therefore identified the junction as a tricritical point.³

Our thermodynamic calculations for the liquid mixtures are based on the expression

$$dg = -sdT + vdP + \phi dx,$$

where g is a molar free energy, s the molar entropy, T the temperature, v the molar volume, P the pressure, ϕ the difference $\mu_3 - \mu_4$ between molar chemical potentials, and x the mole fraction of He^3 . Because of the occurrence of phase separation at temperatures below T_0 , it turns out to be possible in principle to obtain a complete thermodynamic picture of the junction region at saturated vapor pressure almost

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entirely from measurements of the molar specific heat $c_{P,x}$ of the liquid in that region by themselves. Such a determination would not be possible for a liquid which remained everywhere homogeneous. As a result we have been able to make numerical calculations of the quantities $(\partial s/\partial T)_{P,x} = c_{P,x}/T$, $(\partial \phi/\partial T)_{P,x} = -(\partial s/\partial x)_{P,T}$, s , and $\phi - \phi_o$ in the junction region as functions of T and x at saturated vapor pressure. The only additional data needed were two constants and the dependence of molar volume and saturated vapor pressure upon T and x . The constants, $(d\phi/dT)_{\sigma;o}$ and $x_o(d\mu_3/dT)_{\sigma;o} + (1-x_o)(d\mu_4/dT)_{\sigma;o}$ were evaluated using low temperature data discussed in Ref. 1. The path of differentiation indicated by $()_{\sigma}$ here is the phase-separation curve; the subscript o indicates the value at the tricritical point. Because of the smallness of saturated vapor pressure in the junction region, the terms involving the vapor pressure and the molar volume represent corrections to the main terms of the order of only one percent.

It would have been of considerable interest to complete the picture by computing the derivative $(\partial \phi/\partial x)_{P,T}$ throughout the junction region. This derivative was, in fact, already known along the phase-separation curve from the work of Ref. 1. However, because of the accumulation of error resulting from the succession of differentiations and integrations of the data involved, it did not seem likely that enough detail could be preserved to make the process worthwhile.

The results of our calculations can be used to discuss a number of features of the critical behavior of the mixtures near the λ -curve and the tricritical point. At the λ -curve our measurements indicated that

$c_{P,x}$ is finite and continuous but that it has an infinite slope at values of x not too close to x_0 .¹ These findings are in agreement with those of Gasparini and Moldover at lower values of x .⁴ The question which arises immediately is whether the complementary specific heat $c_{P,\phi}$ diverges at the λ -curve as does c_P for pure He⁴. If so, the behavior of $c_{P,x}$ would be an example of the renormalization of the "ideal" behavior of $c_{P,\phi}$ discussed by Fisher.⁵

We have investigated this question indirectly. At the tricritical point it can be shown that the vanishing of $(\partial\phi/\partial x)_{P,T}$ at that point indicated by the results of our specific heat measurements¹ implies the divergence of $c_{P,\phi}$ there. Along the λ -curve it can be shown that $c_{P,\phi}$ diverges if and only if $(\partial s/\partial T)_{P,x} = c_{P,x}/T$ attains its upper bound of $(ds/dT)_{P,\lambda} + (d\phi/dT)_{P,\lambda} (dx/dT)_{P,\lambda}$. Here the path of differentiation indicated by $()_{P,\lambda}$ lies in the λ -surface at constant pressure. A comparison between our determinations of $(\partial s/\partial T)_{P,x}$ and its upper bound is shown in Fig. 1. The curves for $(\partial s/\partial T)_{P,x}$ terminate at ± 1 m°K away from the λ -curve. From this plot we see that it is plausible but by no means established by our data that $(\partial s/\partial T)_{P,x}$ reaches its upper bound at values of x away from x_0 . Hence although it seems likely, we cannot be sure from our data that $c_{P,\phi}$ diverges all along the λ -curve, as it does at $x = 0$ and $x = x_0$.

Near the tricritical point our results are consistent with the following asymptotic behaviors:

$$(\partial s / \partial T)_{P, x; 0} - (\partial s / \partial T)_{P, x} \sim (T - T_0)^1 \text{ along } x = x_0 \text{ for } T > T_0 \quad (\alpha_0 = -1),$$

$$|x - x_0| \sim (T_0 - T)^1 \text{ along } \sigma_{\pm} \text{ for } x \gtrless x_0 \quad (\beta_{\pm} = 1),$$

$$(\partial \phi / \partial x)_{P, T} \sim (T_0 - T)^1 \text{ along both } \sigma_{\pm} \text{ for } T < T_0 \quad (\gamma'_{\pm} = 1),$$

$$(d\phi / dT)_P \sim |T - T_0|^1 \text{ along both } \sigma \text{ and } \lambda\text{-curves} \quad (\phi'_c, \phi_c = 2),$$

$$|\phi - \phi_0| \sim |x - x_0|^2 \text{ along } T = T_0 \text{ for } x \gtrless x_0 \quad (\delta_{\pm} = 2),$$

$$(\partial s / \partial T)_{P, \phi} \sim |T - T_0|^{-1/2} \text{ along } \phi = \phi_0 \text{ for } T \lesseqgtr T_0 \quad (\alpha'_t, \alpha_t = \frac{1}{2}).$$

Here σ_{+} and σ_{-} stand for ^{the} He^3 -rich and He^3 -poor branches of the phase-separation curve, respectively. The exponents in parentheses follow the notation convention recently proposed by Griffiths, with the exception that we introduce two crossover exponents ϕ'_c and ϕ_c in place of his single exponent ϕ to allow for possible differences between the $T < T_0$ and $T > T_0$ cases, respectively.⁶ The subscript c is added in order to distinguish the crossover exponents from our variable ϕ .

Of these six relationships the first three come most directly from experimental data. The first of these was determined from data having a resolution of $\sim 1 \text{ m}^{\circ}\text{K}$. Although our preferred value for α_0 is 1.0, a value as low as 0.8 is possible for a somewhat unlikely alternate interpretation of the data. The second relationship was determined from the phase diagram and the third from the jump in $c_{P, x}$ at the phase-separation curve. Because of the relatively large gaps in x-value at which data were taken, the uncertainties in our determinations of β_{+} , β_{-} , γ'_{+} and γ'_{-} are perhaps several tenths.

The fourth relationship was determined by calculations of $(d\phi/dT)_P$ along the σ and λ -curves. The crossover exponents ϕ_c' and ϕ_c are known from our work only with considerable uncertainty. The evidence for the behavior described by the fifth relationship is shown in Fig. 2, where the continuous curves represent our determinations of $|\phi - \phi_0|$ versus $|x - x_0|$ along the critical isotherm and the dashed curves the determinations of Goellner and Meyer from vapor pressure measurements.⁷ The two determinations agree reasonably well with an exponent of 2, but our values of $|\phi - \phi_0|$ are consistently larger in magnitude than theirs by up to a factor of two. Finally, the evidence for the behavior described by the sixth relationship is shown in Fig. 3. Here $(\partial s / \partial T)_{P, \phi}$ has been constructed along the curve of constant ϕ passing through the tricritical point. Note that the effective temperature resolution here is greater by more than an order of magnitude than the actual experimental temperature resolution available for the measurement of $c_{P, x}$. This increase is due to the flatness of the curve $\phi = \phi_0$ near the tricritical point in the T, x plane, particularly for $x < x_0$.

We note that α_t' , $\alpha_t = 1/2$ represents a stronger divergence of $(\partial s / \partial T)_{P, \phi}$ at the tricritical point than the near-logarithmic divergence seen at the other end of the λ -curve. This breakdown of universality along the λ -curve, at least near the tricritical point, appears to be in accord with recent proposals for scaling near the tricritical point.⁶ Furthermore, we note that all of the above exponents are in agreement with Griffiths's scaling relations/ for the tricritical point. Finally, we note that α_0 satisfies the Fisher renormalization relation with respect to α_t .⁵

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REFERENCES

1. T. A. Alvesalo, P. M. Berglund, S. T. Islander, G. R. Pickett, and W. Zimmermann, Jr., Phys. Rev. A 4, 2354 (1971).
2. For a more complete account of this work see S. T. Islander and W. Zimmermann, Jr., Phys. Rev. A (to be published).
3. R. B. Griffiths, Phys. Rev. Letters 24, 715 (1970).
4. F. Gasparini and M. R. Moldover, Phys. Rev. Letters 23, 749 (1969).
5. M. E. Fisher, Phys. Rev. 176, 257 (1968).
6. R. B. Griffiths (submitted for publication in Phys. Rev.).
7. G. Goellner and H. Meyer, Phys. Rev. Letters 26, 1534 (1971).

FIGURE CAPTIONS

- Fig. 1. The derivative $(\partial s/\partial T)_{P,x} = c_{P,x}/T$ at saturated vapor pressure. The continuous curves show $(\partial s/\partial T)_{P,x}$ at five representative values of x , including $x_0 = 0.6735$. The long-dashed curves show $(\partial s/\partial T)_{P,x}$ along the two arms of the phase-separation curve. The short-dashed curve shows $(ds/dT)_{P,\lambda} + (d\phi/dT)_{P,\lambda}(dx/dT)_{P,\lambda}$ along the lambda curve.
- Fig. 2. The quantity $\ln |\phi - \phi_0|$ at saturated vapor pressure versus $\ln |x - x_0|$ for $T = T_0 = 0.871^\circ\text{K}$. The continuous curves show our results, while the dashed curves show the results of Goellner and Meyer.⁷
- Fig. 3. The quantity $\ln (\partial s/\partial T)_{P,\phi} = \ln (c_{P,\phi}/T)$ at saturated vapor pressure versus $\ln |T - T_0|$ for $\phi = \phi_0$. The condition $x < x_0$ corresponds to $T < T_0$ while $x > x_0$ corresponds to $T > T_0$.

Figure 1.

Figure 2.

Figure 3.