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Thermodynamic Relationships at the Tricritical Point in ^{3}He-^{4}He Mixtures*

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An analysis is made of the λ transition, the phase-separation transition, and the relation between the two, for mixtures of liquid ^{3}He and ^{4}He. Stability conditions require that C_x (specific heat at constant x, where x is the mole fraction ratio x_4/x_3 of ^{4}He to ^{3}He) be less than a certain value, or, equivalently, that $(\partial\mu_4/\partial x)_T$ be positive (μ_4 is the chemical potential of ^{4}He). The phase separation occurs when these conditions are violated. The changes in these quantities appear to occur gradually rather than suddenly, as supposed earlier by one of us. The evidence indicates that there is no real critical singularity at the tricritical point. It then seems reasonable to expand thermodynamic functions about each side of the tricritical point separately, and by thermodynamic arguments the relations between the critical exponents β (for the coexistence curve) and δ (for the critical isotherm) can be obtained and compared with observations.

Some years ago one of us[1] considered the effects of the interaction between the primary variables concerned with the order-disorder phenomena associated with a λ transition and certain secondary variables (e.g., pressure P and molal volume V in the case of the λ transition of liquid helium or a magnetic transition). It was shown that, if the value of the specific heat at constant volume C_V (where the volume is a secondary variable) tended to infinity along a λ line, an instability would result, and the λ transition would turn into a first-order transition. It was realized that a sufficiently large finite value of C_V could give rise to an instability, but only recently has it been noted that more satisfactory explanations of observed phenomena can be obtained if this fact is borne in mind.[2]

If Y is any thermodynamic function (Y constant thus defining a locus in a P, T or P, V or V, T diagram), it may be shown that[2]

$$C_V = C_Y - T\left(\frac{\partial P}{\partial T}\right)_Y \left(\frac{\partial V}{\partial T}\right)_Y + T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_Y^2 . \tag{1}$$

Since for thermodynamic stability

$$\left(\frac{\partial P}{\partial V}\right)_T \leq 0 , \tag{2}$$

we see that such stability also demands

$$C_V \leq C_Y - T\left(\frac{\partial P}{\partial T}\right)_Y \left(\frac{\partial V}{\partial T}\right)_Y , \tag{3}$$

a relation derived by Wheeler and Griffiths.[3] The two criteria given by inequalities (2) and (3) are equivalent. If, in any region, one of them tends not to be fulfilled, the other will also not be fulfilled, and instability, manifested by phase separation, will result.

If C_P rather than C_V tends to become infinite along a λ line (which causes no thermodynamic instability), then by taking $Y \equiv C_P$ and recalling that $(\partial P/\partial V)_T$ vanishes when C_P is infinite, we get the equation derived by Buckingham and Fairbank[4]:

$$C_\lambda = C_V + T\left(\frac{dP_\lambda}{dT}\right)\left(\frac{dV_\lambda}{dT}\right) . \tag{4}$$

If C_V along a λ line is smaller than implied by Eq. (4), we may conclude that C_P, though it may become large, remains finite.

Solutions of ^{3}He in ^{4}He present a situation in which a λ line changes suddenly at a definite temperature into a first-order transition, with two liquid phases in equilibrium. The phase transition is indeed an unusual one.[5,6] The λ line meets the coexistence curve at its top, at what Griffiths[7] calls a tricritical point; the coexistence curve consists of two segments which meet at an angle of less than 180° at this point. In the investigation of the solutions, the pressure remains essentially constant (close to zero), and the appropriate secondary variables are the chemical potential μ_4 of ^{4}He and $x = x_4/x_3$, where x_4 and x_3 are the respective mole fractions of ^{4}He and ^{3}He. The analogs of the equations and inequalities already displayed can be developed by substituting $-\mu_4$ for P and x for V. The appropriate Maxwell equation for these new variables is

$$\left(\frac{\partial S}{\partial x}\right)_T = -\left(\frac{\partial \mu_4}{\partial T}\right)_x , \tag{5}$$

where S is the entropy of 1 mole of ^{3}He and x moles of ^{4}He. Equation (1) is replaced by

$$C_x = C_Y + T\left(\frac{\partial \mu_4}{\partial T}\right)_Y \left(\frac{\partial x}{\partial T}\right)_Y - T\left(\frac{\partial \mu_4}{\partial x}\right)_T \left(\frac{\partial x}{\partial T}\right)_Y^2 , \tag{6}$$

where the specific heats also refer to 1 mole of ^{3}He and x moles of ^{4}He. The inequality (3) is replaced by

$$C_x \leq C_Y + T\left(\frac{\partial \mu_4}{\partial T}\right)_Y \left(\frac{\partial x}{\partial T}\right)_Y . \tag{7}$$

This may be applied along the λ line by taking Y constant along that line, becoming

$$C_x \leq C_\lambda + T_\lambda \left(\frac{d\mu_{4,\lambda}}{dT}\right)\frac{dx_\lambda}{dT} . \tag{8}$$

It was suggested by Rice[8] that, at the tricritical point, there was a change from a situation in which $C_{\mu_4,\lambda}$ was infinite to one, in the two-phase region, in which $C_{x,\lambda}$ tended to become infinite. If however the right-hand side of (8) is evaluated roughly with the help of the regular-solution assumption, and compared to measured values of $C_{x,\lambda}$, it appears that the transition is probably much more gradual, with $C_{x,\lambda}$ less than, but gradually approaching, the right-hand side above the tricritical point, and crossing the critical value at that point. This view appears to be supported by recent work of Goellner and Meyer,[9] which indicates that $(\partial\mu_4/\partial x)_T$ approaches zero linearly at the tricritical point and would become negative were it not for the phase separation. However final judgment should be withheld until high-resolution data are available close to the λ line.

The results of Goellner and Meyer bring to mind certain thermodynamic relationships obtained in a different connection.[10] These relationships were specifically for liquid-vapor systems; for the ^{3}He-^{4}He system we need to use the appropriate variables defined above.

Following Ref. 10, but using the new variables, we first note that

$$\frac{\partial^2\mu_4}{\partial T \partial x} = -\left(\frac{\partial^2\mu_4}{\partial T^2}\right)_x \left(\frac{\partial T}{\partial x}\right)_{(\partial\mu_4/\partial T)_x} , \tag{9}$$

which is obtained by considering $(\partial\mu_4/\partial T)_x$, T, and x as the three interdependent variables to which to apply one of the standard formulas of partial differentiation. It was believed that $\partial^2\mu_4/\partial T\partial x$ (actually its equivalent $\partial^2 P/\partial T\partial V$) was not zero at a critical point, which would mean that contours of constant $(\partial\mu_4/\partial T)_x$ would not lie parallel to the x axis in an x-T diagram. Thus $(\partial T/\partial x)_{(\partial\mu_4/\partial T)_x}$ could not be zero, and $(\partial^2\mu_4/\partial T^2)_x$ could not be infinite. By Eq. (5),

$$\left(\frac{\partial^2\mu_4}{\partial T^2}\right)_x = -\frac{\partial^2 S}{\partial x \partial T} , \tag{10}$$

and we conclude that the right-hand side of Eq. (10), and hence $(\partial S/\partial T)_x$ and the specific heat at constant mole fraction (of the 1 mole of ^{3}He and x moles of ^{4}He) C_x must remain finite. At any normal critical point of a binary liquid system it is now believed (overlooking "renormalization," which is not relevant here) that C_x actually does become infinite. Therefore we may conclude that $\partial^2\mu_4/\partial T\partial x$ must vanish at a critical point, as appears to be observed for the analogous quantity $\partial^2 P/\partial T\partial V$ in a liquid-vapor system.

However, at the tricritical point in ^{3}He-^{4}He solutions it appears that C_x does *not* become infinite, and there is no reason to believe that $\partial^2 S/\partial x\partial T$ becomes infinite. Unfortunately, it seems impossible to prove the converse of the above theorem, so that it is not possible to show that if $\partial^2 S/\partial x\partial T$ remains finite $\partial^2\mu_4/\partial T\partial x$ does not become zero. The results of Goellner and Meyer indicate, however, that $\partial^2\mu_4/\partial T\partial x$ does not vanish at the tricritical point (at least on the ^{3}He-rich side), this being equivalent to setting the critical exponent γ equal to 1. [Actually they show that $\partial^2(\mu_4-\mu_3)/\partial T\partial x_3$ does not vanish. But since, at constant T, by the Gibbs-Duhem relation, $d\mu_4 - d\mu_3 = x_3^{-1}\, d\mu_4$, and since $dx = -x_3^{-2}\, dx_3$, it is seen that their result implies $\partial^2\mu_4/\partial T\partial x \neq 0$.] This result, while not required by the thermodynamics, is consistent with it.

The linear behavior of $(\partial\mu_4/\partial x)_T$ certainly suggests that there is not a singularity at the tricritical point in the same sense as at a critical point. If there were no λ line, the phase separation would presumably exhibit the usual type of critical phenomenon at some temperature lower than the tricritical temperature. Any critical mixing point exerts some destabilizing influence in the one-phase region above it, as evidenced by the lowered slope of the isotherms. The presence of the λ line also tends to lower the slope of the isotherms, and we may suppose that these two influences together cause the slope to vanish at a higher temperature and to tend to cross over into the negative region without introducing any singularity other than the discontinuities characteristic of the λ line. Although certain rather strange coincidences occur at the λ line, which we will discuss later, we shall on this basis apply the reasoning of Ref. 10, which involved expanding the entropy in Taylor's series on either side of the tricritical point. The indications are that the derivatives $\partial^2 S/\partial T^2$, $\partial^2 S/\partial x\partial T$, and $\partial^2 S/\partial x^2 = -\partial^2\mu_4/\partial T\partial x$, necessary for the expansions, are all finite and nonzero at the tricritical point. Of course, these quantities seem to be discontinous along the λ line, and this indicates singularities in the higher derivatives, but there is no reason to expect the latter singularities to be foreshadowed as the tricritical point is approached; indeed, they appear to become less marked or to vanish at the tricritical point. Using total derivatives to indicate changes along the coexistence curve, i.e., the boundary between the two-phase and one-phase regions, we start with the relation

$$\frac{dx}{dT}=\left(\frac{\partial x}{\partial T}\right)_{\mu_4}+\left(\frac{\partial x}{\partial \mu_4}\right)_T\frac{d\mu_4}{dT}$$

$$=-\left(\frac{\partial x}{\partial \mu_4}\right)_T\left(\frac{\partial \mu_4}{\partial T}\right)_x+\left(\frac{\partial x}{\partial \mu_4}\right)_T\frac{d\mu_4}{dT}\quad . \tag{11}$$

Application of Eq. (5) (including application within the two-phase region, which gives $d\mu_4/dT=-\Delta S/\Delta x$, where ΔS and Δx are the differences of S and x between phases in equilibrium with each other) gives the analogy of Eq. (5) in the previous article[10]:

$$\frac{dT}{dx}=\left(\frac{\partial \mu_4}{\partial x}\right)_T\left[\left(\frac{\partial S}{\partial x}\right)_T-\frac{\Delta S}{\Delta x}\right]^{-1}. \tag{12}$$

Proceeding with the expansion of S along the coexistence curve on the ^{3}He-rich side (subscript a) about the tricritical point (subscript t), we can write

$$S_a=S_t+\left(\frac{\partial S}{\partial x}\right)_{T,t}(x_a-x_t)+\left(\frac{\partial S}{\partial T}\right)_{x,t}(T-T_t)$$

$$+\frac{1}{2}\left(\frac{\partial^2 S}{\partial x^2}\right)_{T,t,a}(x_a-x_t)^2$$

$$+\left(\frac{\partial^2 S}{\partial x\,\partial T}\right)_{t,a}(x_a-x_t)(T-T_t)$$

$$+\frac{1}{2}\left(\frac{\partial^2 S}{\partial T^2}\right)_{x,t,a}(T-T_t)^2+\cdots\quad . \tag{13}$$

To reduce to a single variable we shall set $T-T_t=(dT/dx)_{t,a}(x_a-x_t)$. Had we been able to follow the procedure in Ref. 10 in complete detail, we would have set $(dT/dx)_{t,a}=0$, but this is, of course, not possible at the tricritical point. Along the ^{4}He-rich side (subscript b) we will get an entirely similar expression if we substitute subscript b for subscript a. The value of $C_{x,t}/T_t=(\partial S/\partial T)_{x,t}$ does not depend on which side of the coexistence curve we approach the tricritical point from, and the same is true of $(\partial S/\partial x)_{T,t}$, [see the discussion of Eqs. (17) and (18) below] but the second derivatives may depend on the side of the coexistence curve. From Eq. (13) and its analog we get

$$\frac{\Delta S}{\Delta x}=\frac{S_a-S_b}{x_a-x_b}\approx\left(\frac{\partial S}{\partial x}\right)_{T,t}+\frac{1}{2}\frac{(x_a-x_t)^2}{x_a-x_b}\left[\left(\frac{\partial^2 S}{\partial x^2}\right)_{T,t,a}+2\left(\frac{\partial^2 S}{\partial x\partial T}\right)_{t,a}\left(\frac{dT}{dx}\right)_{t,a}+\left(\frac{\partial^2 S}{\partial T^2}\right)_{x,t}\left(\frac{dT}{dx}\right)^2_{t,a}\right]$$

$$-\frac{1}{2}\frac{(x_b-x_t)^2}{x_a-x_b}\left[\left(\frac{\partial^2 S}{\partial x^2}\right)_{T,t,b}+2\left(\frac{\partial^2 S}{\partial x\partial T}\right)_{t,b}\left(\frac{dT}{dx}\right)_{t,b}+\left(\frac{\partial^2 S}{\partial T^2}\right)_{x,t,b}\left(\frac{dT}{dx}\right)^2_{t,b}\right]=\left(\frac{\partial S}{\partial x}\right)_{T,t}+K(x_a-x_b)\ , \tag{14}$$

where K is a constant, since x_a-x_t and x_b-x_t will be, in first order, proportional to x_a-x_b.

Expanding $(\partial S/\partial x)_{T,a}$ we get

$$\left(\frac{\partial S}{\partial x}\right)_{T,a}\approx\left(\frac{\partial S}{\partial x}\right)_{T,t}+\left(\frac{\partial^2 S}{\partial x^2}\right)_{T,t,a}(x_a-x_t)$$

$$+\left(\frac{\partial^2 S}{\partial x\partial T}\right)_{t,a}\left(\frac{dT}{dx}\right)_{t,a}(x_a-x_t)$$

$$=\left(\frac{\partial S}{\partial x}\right)_{T,t}+K'_a(x_a-x_b) \tag{15}$$

and similarly for $(\partial S/\partial x)_{T,b}$. Since $(\partial S/\partial x)_{T,t}$ cancels, we see that the bracket in Eq. (12) is proportional to x_a-x_b, x_a-x_t, or x_b-x_t. Thus it is seen from Eq. (12) that if

$$\mu_4-\mu_{4,t}\propto(x-x_t)^\delta$$

at constant T, and

$$T-T_t\propto(x-x_t)^{1/\beta}$$

along the coexistence curve, then

$$\delta=\beta^{-1}+1\ , \tag{16}$$

which is equivalent to the relation obtained before.[10] Since $\beta^{-1}=1$, we see that δ should be equal to 2. This is the conclusion that follows, within limits of error, from the data of Goellner and Meyer. It is the same as would be calculated from the relation $\gamma=\delta-1$ obtained by Griffiths from an assumed scaling function (written $\epsilon=\mu^{-1}-1$ by him), if we set $\gamma=1$, as was indeed pointed out by Goellner and Meyer.

The agreement obtained by the above with the experimental data for the phase separation of ^{3}He-^{4}He mixtures suggests that this system may be one in which it is legitimate to apply the discussion of Ref. 10, expanding thermodynamic functions about the critical point (using separate expansions on each side of it), and obtaining exact relations between the critical (tricritical) exponents by thermodynamic deductions. There are, however, several peculiar features which ought to be considered.

We have noted that the second derivatives of S may be different on the two sides of the λ line. An examination of Goellner and Meyer's figure seems in fact to indicate that on the ^{4}He-rich side of the λ line the μ_4 vs x curves are very closely parallel and are uniformly spaced in the T direction. To the extent that this is true, $\partial^2\mu_4/\partial x\partial T$ and $(\partial^2\mu_4/\partial T^2)_x$, and hence $(\partial^2 S/\partial x^2)_T$ and $\partial^2 S/\partial x\partial T$, vanish on the ^{4}He-rich side in the neighborhood of the tricritical point. In itself, this would not affect our conclusions, since it would not affect the general behavior of the bracket of Eq. (12), but it is a peculiarity which any complete theory should account for.

If the μ_4 vs x curves are parallel parabolic curves, then it is seen that the tricritical point occurs where the λ line crosses the apex of one of the parabolas. It seems somewhat strange that this should occur just where $(\partial\mu_4/\partial x)_T$ vanishes on the other side of the λ line, especially as it can be seen that there is a break in $(\partial\mu_4/\partial x)_T$ at the λ line at temperatures slightly above the tricritical temperature. It would be necessary for $(\partial\mu_4/\partial x)_T$ to become zero on one side only of the λ line in order for an instability, necessitating a phase separation, to occur. The thermodynamics of such a situation can be readily worked out.

The λ line is one across which there is no discontinuity in μ_4 or S; therefore we can write, along the λ line,

$$dS=\left(\frac{\partial S}{\partial x}\right)_{T,a}dx+\left(\frac{\partial S}{\partial T}\right)_{x,a}dT$$

$$=\left(\frac{\partial S}{\partial x}\right)_{T,b}dx+\left(\frac{\partial S}{\partial T}\right)_{x,b}dT\ , \tag{17}$$

$$d\mu_4=\left(\frac{\partial \mu_4}{\partial x}\right)_{T,a}dx+\left(\frac{\partial \mu_4}{\partial T}\right)_{x,a}dT$$

$$=\left(\frac{\partial \mu_4}{\partial x}\right)_{T,b}dx+\left(\frac{\partial \mu_4}{\partial T}\right)_{x,b}dT\ . \tag{18}$$

The derivatives of S and μ_4 are connected by Eq. (5). From Eqs. (5), (17), and (18) we see that, if any one of the derivatives $(\partial S/\partial x)_T$, $(\partial S/\partial T)_x$, $(\partial\mu_4/\partial x)_T$, $(\partial\mu_4/\partial T)_x$ is continuous across the λ line, they must all be, and if one has a discontinuity, they all do, the discontinuities being, of course, connected by Ehrenfest-type relations. If there is a discontinuity in $(\partial S/\partial x)_T$ at the tricritical point, so that $(\partial S/\partial x)_{T,t,a}\neq(\partial S/\partial x)_{T,t,b}$, these terms will not cancel in the bracket in Eq. (12), and instead of Eq. (16) we would find

$$\delta=\beta^{-1}\ . \tag{19}$$

On the side of the coexistence curve where $(\partial\mu_4/\partial x)_T$ did not vanish we would have $\delta=1$ and so $\beta=1$. On the other side of the coexistence curve or the λ line, where $(\partial\mu_4/\partial x)_T$ vanishes $\delta=2$ and therefore $\beta=\frac{1}{2}$. Such a situation would be inconsistent with a tricritical point as it appears to be observed.

The fact that there appears to be no break in C_x across the λ line in the immediate neighborhood of the tricritical point also indicates that $(\partial\mu_4/\partial x)_T$ has the same (zero) value on the two sides of the tricritical point. However, the isotherms on the ^{4}He-rich side are so flat over a considerable range of x that if the zero values on the two sides missed each other a little it might not be noticed. It is, however, remarkable that not only is there no break in C_x, but that the cusp in C_x seems to disappear at the tricritical point. Thus at this composition there is one continuous specific-heat curve, with possibly a slight break in the slope. There is a tendency to think that the λ transition has become very weak at this point, but this appearance is deceptive. There is still a very substantial drop in the specific heat as the temperature is raised into the nonsuperfluid region, which means that there must be an order-disorder phenomenon occurring at the low-temperature end of the λ line, which is not substantially less important than that which occurs when the λ line is crossed at higher T_λ and lower ^{3}He concentrations. It is merely true that part of the order-disorder transition occurs in the two-phase region, and the two parts have become merged, so possibly there is nothing essentially different about the low-temperature end of the λ transition. The separation into two phases occurs because the stability limits of the thermodynamic quantities C_x and $(\partial\mu_4/\partial x)_T$ have been reached.

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