Critical Phenomenon and Phase Separation in ^{3}He-^{4}He Mixtures

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(May 5, 1998)

Abstract

This paper is a brief survey of ^{3}He-^{4}He mixtures, with special attention to critical phenomenon. The phase diagram in the T-X plane is discussed, as well as the ability of phenomenological Landau theory to explain it. Landau theory is then applied to the T-ϕ plane, with more successful results. The Siggia-Nelson model is briefly mentioned. Finally, the details of phase separation are presented, with discussion about the meaning and derivation of the spinodal lines which bound the unstable and metastable parts of the two phase region.

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I. INTRODUCTION

Anyone interested in critical phenomenon would be foolish not to investigate ^{3}He-^{4}He mixtures, even if just briefly. The concepts of phase transitions, tricritical behavior, scaling, and universality are all used, in conjunction with tools like mean field theory and the renormalization group, to explain this seemingly simple system. The system has a variety of practical applications as well, either as a model system to help explain binary fluid mixtures and alloys, or as a tool to experimentally examine molecules in an effective vacuum [11]. This paper will primarily discuss the phase diagram of ^{3}He-^{4}He , and the best attempts of mean field theory, namely Landau theory, to partially explain it, as well as some of the details of phase separation.

II. CRITICAL BEHAVIOR

A. ^{3}He-^{4}He T-X Phase Diagram

The phase diagram for ^{3}He-^{4}He is most commonly presented in the T-X plane (see figure 1), where X is the relative ^{3}He concentration:

$$X = \frac{N_3}{N_3 + N_4} \tag{1}$$

At X=0, the phase diagram simply shows the phase behavior of ^{4}He, with a second-order phase transition from a normal fluid to a superfluid at T_λ. The addition of ^{3}He decreases the transition temperature at which the mixture becomes superfluid, making it a function of X, and giving rise to the so-called "λ line", the line of second-order superfluid phase transitions.

If we treat ^{4}He as an ideal degenerate Bose-Einstein gas, and ^{3}He as a Fermi-Dirac gas, then it is possible to calculate the X-dependence of T_λ to be

$$T_\lambda(X) = T_{\lambda 0}(1-X)^{\frac{2}{3}} \tag{2}$$

This form of T_λ, although not exact for real mixtures of ^{3}He-^{4}He , yields derivatives of T with respect to X which agree closely with experimental results near X=0 [1]. The λ line terminates at a tricritical point, below which the mixture phase separates. (The tricritical point in ^{3}He-^{4}He is located at $X_t = 0.675 \pm 0.001$ and $T_t = 0.8671 \pm 0.001\ K$ [1].) The two-phase region is bounded by two first-order phase transitions into the superfluid and normal phases, respectively. Phase separation and the two-phase region will be discussed at more length in section III.

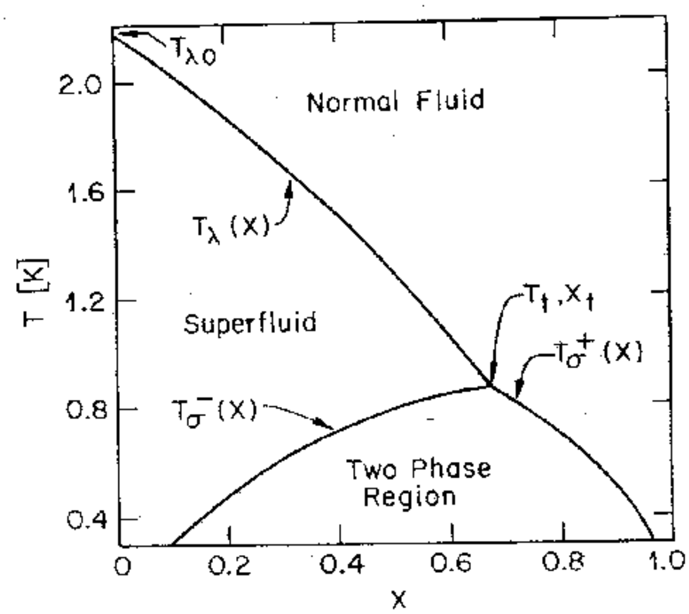

Figure 1: T-X Phase Diagram of ^{3}He-^{4}He [1]

It should be noted that the accepted ^{3}He-^{4}He phase diagram comes solely from experimental results. Although several different regions of the phase diagram can be well-explained by theory, including the zero temperature region, the λ line, and the region surrounding the tricritical point, no theory has yet been able to predict the full phase diagram.

B. Landau Theory in the T-X plane

Phenomenological Landau theory is a mean-field technique that can often be used to successfully describe the macroscopic behavior of systems near critical points [9,10]. The reader should already be familiar with the application of Landau theory to the η^6 model, whose Landau free energy can be written as

$$L = \frac{1}{2}a\eta^2 + \frac{1}{4}b\eta^4 + \frac{1}{6}c\eta^6 - h\eta \tag{3}$$

where η is the order parameter, $h = \frac{H}{k_b T}$, c is a positive constant and a and b are functions of pressure and temperature. In ^{3}He-^{4}He mixtures, Landau theory yields accurate qualitative information about the phase behavior near the tricritical point.

Let us assume the following scaling behavior near the tricritical point

$$x \equiv \left| \frac{X_t - X_\sigma}{X_t} \right| = B \left(\frac{T_t - T_\sigma}{T_t} \right)^\beta \tag{4}$$

where X_t and T_t are the concentration and temperature at the tricritical point. Landau theory predicts that $\beta = 1$ for both first-order phase boundaries T_{σ^+} and T_{σ^-}, which is found to be true experimentally near the tricritical point [1]. Hence, the phase boundaries should be linear in the region where x is small, and Landau theory can also be used to estimate their slope. As shown in figure 2, Landau theory correctly calculates the slope of T_{σ^-} to be $B_-^{Landau} = 4.19$, but predicts that the slope of T_{σ^+} will be the same as the slope of T_λ, giving a value of $B_+^{Landau} = 0.52$. This does not match experimental observations of $B_+^{expt} = 0.88$ near the tricritical point.

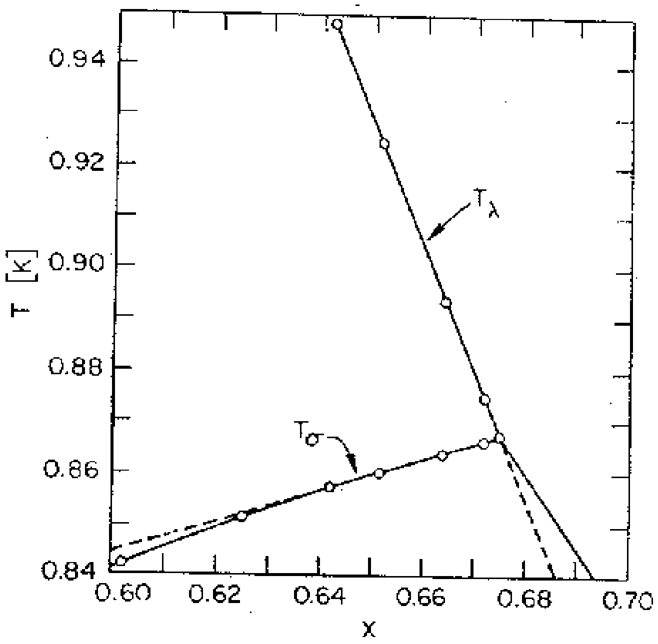

Figure 2: T-X Phase Diagram, near the tricritical point [1]. The dotted lines indicate the predictions of phenomenological Landau Theory

C. Landau Theory in the T-ϕ plane

Griffiths [7] proposed that phenomenological Landau theory could not be applied to a system with a tricritical point in the same way it was to systems with "ordinary" critical points. To illustrate this, he proposed a different approach. He replaced the variable X with the intensive variable $\phi \equiv \mu_3 - \mu_4$, which is defined as the difference in the chemical potentials of the two isotopes, and calculated the phase diagram in the T-ϕ plane. The phase diagram which Landau theory predicts in the T-ϕ plane has several convenient properties. The T_σ line is a smooth continuation of the T_λ line, and only has one branch, since the two phases have the same chemical potential when in equilibrium. Most importantly, this phase diagram seems to correspond with experimental results [1]. If you introduce the field η, which is the field conjugate to the superfluid order parameter $|\psi|$ ($\eta \equiv \frac{\partial F}{\partial |\psi|}$), then the phase diagram in $T\phi\eta$ space shows two critical coexistence lines intersecting the λ line at the tricritical point. (It was this unique property that led Griffiths to propose the name "tricritical point" for the critical point associated with ^{3}He-^{4}He mixtures, as well as other systems with the same property.) It should be noted that $\eta \neq 0$ is experimentally inaccessible. Griffiths used this analysis to propose a scaling function for the free energy which yields a phase diagram in the T-X plane whose right coexistence curve near the tricritical point no longer has the same slope as the λ line, but rather has a distinct slope which is more consistent with the experimental phase diagram in that plane.

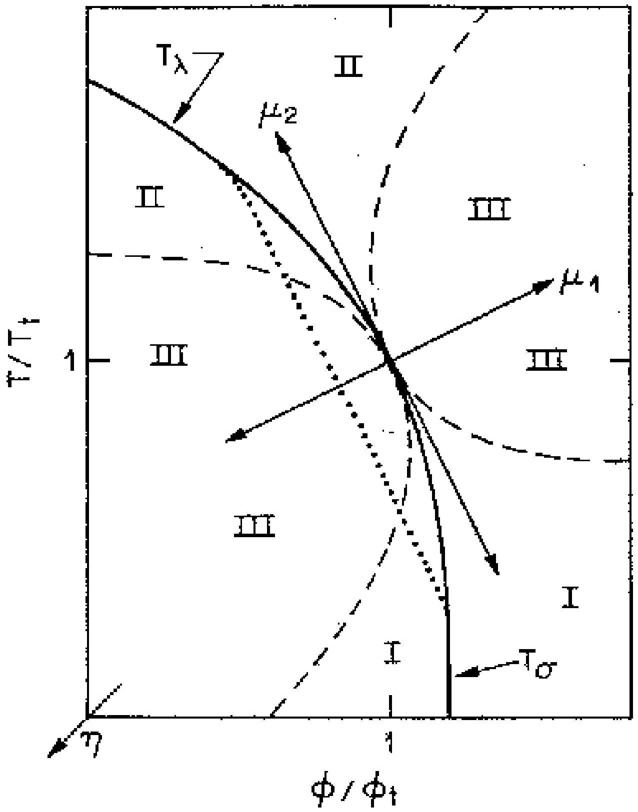

Figure 3: T-ϕ Phase Diagram of ^{3}He-^{4}He [1]. Regions I,II, and III are discussed in the text.

Riedel [8] proposed two scaling fields μ_1 and μ_2 (not to be confused with chemical potential), which are linear combinations of $T - T_t$ and $\phi - \phi_t$

$$\mu_1 = \frac{\phi - \phi_t}{\phi_t}; \quad \mu_2 = \frac{T - T_t}{T_t} \tag{5}$$

At the tricritical point, $\mu_1 = \mu_2 = 0$, the μ_2 axis is tangential to T_λ, and the μ_1 axis is perpendicular to them both (see figure 3). Using these fields, the λ line can be written as

$$\mu_1 = -r_\lambda \mu_2^{1/\varphi} \tag{6}$$

where r_λ is a positive constant, and φ is the so-called "crossover exponent". Experimental results are consistent with this form, and φ has been calculated to be $\frac{1}{2}$.

Riedel also split the T-ϕ phase diagram up into three different regions, labelled I-III, to denote the different critical behavior of each region. Region I corresponds to the system being near a first-order transition. Region II corresponds to the system being near a second-order transition (in this case the superfluid transition). Region III is dominated by the tricritical behavior. In region II, the character of the transition does not depend on ϕ which suggests that universality applies in this region. The dashed lines which define the boundaries between the regions in figure 3 have the same scaling form as the λ line

$$\mu_1 \propto \mu_2^{1/\varphi} \tag{7}$$

and are thus tangential to it at the tricritical point. It should be noted that these lines are not sharp transitions.

D. Siggia-Nelson Model

Although Landau theory can explain the phase diagram and give reasonable estimates for equilibrium behavior, it is insufficient for other areas of critical phenomenon, most notably dynamic critical phenomenon. Hence, many different models were discussed and considered to explain the dynamics of ^{3}He-^{4}He mixtures, as well as other binary mixtures and alloys [5]. The two strongest contenders were the "model C" [5] and the Siggia-Nelson model [3]. (Anyone with an interest in renormalization group theory should study the details of references [3] and [5].) However, the Siggia-Nelson model now seems to be accepted as the model which best describes dynamical properties of ^{3}He-^{4}He mixtures. It was successfully used to calculate the scaling of the mass diffusion coefficient and the dynamic crossover scaling functions [3].

III. PHASE SEPARATION

A. Two Phase Region

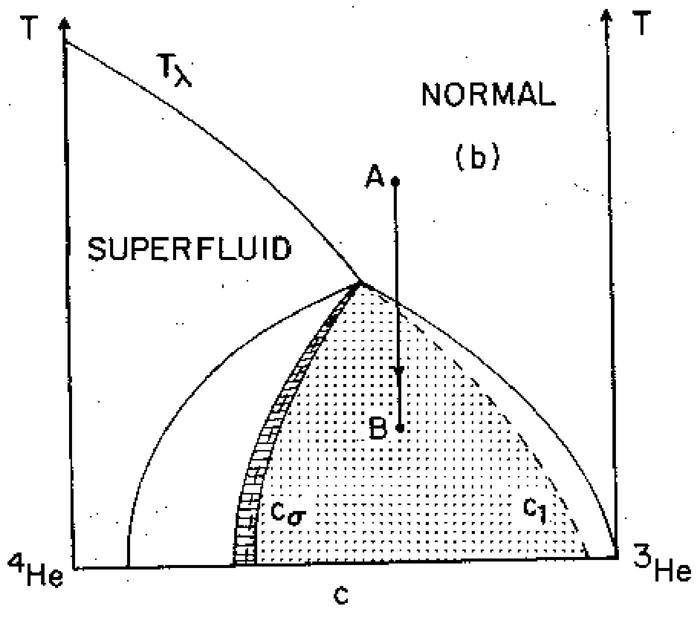

Figure 4: Two phase region of ^{3}He-^{4}He [2]. The unstable spinodal region is shaded, and is bounded by the fuzzy spinodal line c_σ on the left and the somewhat sharper c_1 on the right. c_s and c_n determine the superfluid and normal fluid coexistence lines, respectively.

When a ^{3}He-^{4}He system is quenched into the two phase region of the phase diagram (see figure 4), phase separation occurs. During phase separation, the element which is the minority of the mixture coalesces and forms droplets against a background primarily consisting of the majority element. For example, at $X = 0.70$, because there is more ^{3}He than ^{4}He, ^{4}He-rich superfluid droplets will form in a ^{3}He-rich normal background.

In a normal binary mixture, the two phase region is symmetric, and the phase boundary looks like a parabola. Previous work on normal binary mixtures revealed that the two phase region consists of a metastable region and a "spinodal" region, with fuzzy "spinodal" lines separating the two regions. (The fuzziness of the spinodal lines seems to be an artifact of a system having short-range forces [4].) The only difference between the two regions is the dynamic processes through which the system phase separates when quenched into each region [6]. The spinodal region is unstable to concentration fluctuations, so a quench into the spinodal region will cause phase separation to immediately take place, with the system coarsening into two different phases. Quenching into the metastable region leads to phase separation through homogenous nucleation, or the formation of droplets. Droplet formation in the metastable region depends on some critical radius R_c; droplets whose radius is greater than R_c will grow spontaneously, while droplets whose radius is smaller will shrink.

As we've seen in ^{3}He-^{4}He , the two phase region is asymmetric about the tricritical point, although it does have a somewhat parabolic shape to it. The spinodal region and spinodal lines have a different shape than a normal binary fluid, but share the same general properties [2].

B. Calculating The Spinodal Lines

The mean-field approximation to the free energy is given by [2]

$$F(T,\phi) = min(\frac{1}{2}r|\psi|^2 + u|\psi|^4 + \nu|\psi|^6 + \frac{1}{2}\chi_n^{-1}c^2 + \gamma c|\psi|^2 - \phi c) \tag{8}$$

We want to define the concentration susceptibility

$$\chi_c \equiv \left|\frac{\partial^2 F}{\partial \phi^2}\right|_T \tag{9}$$

where ϕ is the difference in the chemical potential of the two species. When a region is unstable to fluctuations in the concentration, the concentration susceptibility in that region will be negative. The point where χ_c becomes negative defines the spinodal lines.

Hohenberg and Nelson [2] performed the calculation by assuming that the superfluid order parameter, while not conserved, is constrained. Thus it can be determined from the initial values of the concentration, which is conserved, and the temperature. The magnitude of ψ is determined by the following equation:

$$\frac{\partial|\psi|}{\partial t} = -\Gamma\frac{\delta F}{\delta|\psi|} = -\Gamma|\psi|\gamma(c-\bar{c}) \tag{10}$$

where Γ and γ are constants, $|\psi|$ is the superfluid order parameter, and $\bar{c}$ is defined by

$$\bar{c} = -\left[\frac{r}{2\gamma} + \frac{2u}{\gamma}|\psi|^2 + \frac{3\nu}{\gamma}|\psi|^4\right] \tag{11}$$

It follows that the solution in the normal fluid regime ($|\psi| = 0$) is stable only for values of c in the range

$$c_1 < c < c_n \tag{12}$$

where c_1 is defined as

$$c_1 = -r/2\gamma \tag{13}$$

The other spinodal line, which corresponds to the superfluid phase boundary, is more difficult to calculate. The basic calculation involves determining χ_c^{-1} and calculating the value of c at which it goes to zero. χ_c depends on ψ, so the constrained form of χ_c (which we write as $\bar{\chi_c}$) can be calculated and yields the following equation:

$$\bar{\chi_c}(c) = \chi_n, \qquad c_1 < c < c_n \tag{14}$$

$$\bar{\chi_c}(c) = \chi_n \left[\frac{u + 3\nu\psi^{-2}}{-|\tilde{u}| + 3\nu\psi^{-2}} \right], \qquad c_s < c < c_1 \tag{15}$$

The spinodal point c_σ is defined by the concentration at which this equals zero, and is found to be a function of c_n, c_s, and c_1. It can be approximated as

$$c_\sigma \approx \frac{1}{3}c_n + \frac{2}{3}c_s \tag{16}$$

near the tricritical point [2].

IV. CONCLUSIONS

Hopefully this paper has presented a general overview of the basic ideas of critical phenomenon and phase separation in ^{3}He-^{4}He mixtures. This is a rich field, with many unanswered questions, and the reader is encouraged to explore the listed references for more details.

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