PHYSICAL REVIEW VOLUME 124, NUMBER 3 NOVEMBER 1, 1961

Phase Separation in He^3-He^4 Mixtures near Absolute Zero

D. O. EDWARDS AND J. G. DAUNT
Department of Physics and Astronomy, Ohio State University, Columbus, Ohio

(Received June 26, 1961)

Phase separation in liquid mixtures of He^3 and He^4 at temperatures close to 0°K is discussed on the basis of the isotopic impurity models of Pomeranchuk and Zharkov and Silin. It is predicted that for He^3-rich mixtures the phase separation line is asymptotic to the temperature axis as $T \rightarrow 0$, so that phase separation should occur in extremely dilute solutions of He^4 in He^3 at relatively high temperatures. For example, 0.003% of He^4 in liquid He^3 should begin to separate at about 0.1°K. The phase separation curve for He^4-rich mixtures near 0°K is difficult to predict with the data available at present. One possibility is that dilute solutions of He^3 in He^4 may be stable at 0°K.

It has recently been shown by De Bruyn Ouboter, Taconis, Le Pair, and Beenakker[1] that the thermodynamic functions and phase diagram for liquid He^3-He^4 mixtures above 0.4°K are in good agreement with the theories of Pomeranchuk[2] and of Zharkov and Silin,[3] provided that the concentration of one of the components is not too large. Since both theories are intended to apply to dilute mixtures at temperatures close to 0°K, they may be used with some confidence to discuss the form of the phase separation line at very low temperatures, i.e., below 0.4°K, the lowest temperature at which reliable measurements have been made.

Phase separation in very dilute solutions of He^4 in He^3 is of some practical interest at the moment, since a number of experiments on liquid He^3 at extremely low temperatures have recently been made or are planned. Many of these are concerned with properties of the liquid which may be modified by the small amounts of He^4 impurity which are usually present in "pure" He^3. For instance, at very low temperatures the mean free path of the quasi-particles may be limited by collisions with He^4 atoms, which may affect the experimental values of the transport coefficients or may inhibit the transition to the recently proposed superfluid state.[4] Alternatively, phase separation of the He^4 impurity may produce small anomalies in the apparent thermodynamic functions of the "pure" liquid.[1] It is shown in this note that according to the theory of Zharkov and Silin the phase separation line at very low temperatures lies much closer to the temperature axis than might be expected from presently available experimental data, so that phase separation at very low concentrations of He^4 will take place within the experimentally accessible temperature range. However, the phase separation may have favorable results in some experiments by purifying the He^3-rich phase, although the presence of a small volume of the superfluid, He^4-rich phase might be objectionable.

For very dilute solutions of He^3 in He^4, the theory of Pomeranchuk indicates that the phase separation line may not pass through the origin of the phase diagram, so that a mixture of the isotopes may be stable at 0°K. It would be of some theoretical interest to discover whether this possibility is realized experimentally.

In a phase-separated mixture of He^3 and He^4 the chemical potential of each isotope must be the same in the upper and lower phases:

$$\begin{aligned} \mu_3(X_l,T)&=\mu_3(X_u,T), \\ \mu_4(X_l,T)&=\mu_4(X_u,T). \end{aligned} \tag{1}$$

(X_l and X_u are molar concentrations of He^3 in the lower and upper phases.) The experimental results indicate that at sufficiently low temperatures, X_l and $(1-X_u)$ become small enough for the He^4 in the upper phase and the He^3 in the lower phase to be treated as impurities of very low concentrations. The chemical potentials $\mu_4(X_u,T)$ and $\mu_3(X_l,T)$ can then be calculated from the Zharkov and Silin and Pomeranchuk theories. Both theories treat isotopic impurities in helium as independent particles with energy-momentum relations of the form

$$\begin{aligned} \epsilon_3&=-E_3+p^2/2m_3^* \quad \text{(Pomeranchuk)}, \\ \epsilon_4&=-E_4+p^2/2m_4^* \quad \text{(Zharkov and Silin)}, \end{aligned} \tag{2}$$

where $-E_3$ and $-E_4$ are the binding energies of the impurity isotopes and m_3^*, m_4^* their effective masses. The chemical potentials follow immediately from statistical mechanics[5]:

$$\begin{aligned} \mu_3{}^l&=RT\ln\left\{\frac{NX_l}{V_l(kT)^{\frac{3}{2}}}\frac{h^3}{2(2\pi m_3^*)^{\frac{3}{2}}}\right\}-NE_3, \\ \mu_4{}^u&=RT\ln\left\{\frac{N(1-X_u)}{V_u(kT)^{\frac{3}{2}}}\frac{h^3}{(2\pi m_4^*)^{\frac{3}{2}}}\right\}-NE_4, \end{aligned} \tag{3}$$

assuming that the concentrations X_l and $(1-X_u)$ are

---

[1] R. de Bruyn Ouboter, K. W. Taconis, C. Le Pair, and J. J. M. Beenakker, Physica **26**, 853 (1960).

[2] I. J. Pomeranchuk, J. Exptl. Theoret. Phys. (USSR) **19**, 42 (1949).

[3] V. N. Zharkov and V. P. Silin, J. Exptl. Theoret. Phys. (USSR) **37**, 143 (1959) [translation: Soviet Phys.—JETP **10**, 102 (1960)].

[4] K. A. Brueckner, T. Soda, P. W. Anderson, and P. Morel, Phys. Rev. **118**, 1442 (1960); L. P. Pitaevskii, J. Exptl. Theoret. Phys. (USSR) **37**, 1794 (1959) [translation: Soviet Phys.—JETP **10**, 1267 (1960)]; V. J. Emery and A. M. Sessler, Phys. Rev. **119**, 43 (1960).

[5] The additional factor of 2 in the equation for $\mu_3{}^l$ accounts for the spin of He^3.

sufficiently small for degeneracy and interaction effects to be negligible. The volumes V_u and V_l are the molar volumes of the upper and lower phases, N is Avogadro's number, and the other symbols have their usual meanings.

To complete Eqs. (1) we need the chemical potentials of the concentrated components $\mu_3{}^u$ and $\mu_4{}^l$. If the impurity concentrations are low enough, the ideal solution form is sufficiently accurate:

$$\begin{aligned}\mu_3(X_u,T)&=G_3{}^0(T)+RT\ln X_u,\\ \mu_4(X_l,T)&=G_4{}^0(T)+RT\ln(1-X_l),\end{aligned}\tag{4}$$

where $G_3{}^0$ and $G_4{}^0$ are the Gibbs potentials of the pure phases. The lowest temperature at which precise measurements of the phase separation concentrations have been made is 0.39°K (Roberts and Sydoriak,[6] De Bruyn Ouboter *et al.*[1]). In this range X_l and $(1-X_u)$ are large enough for significant deviations from (4) to occur. To compare the theory with the experimental results, we therefore modify (4) to the empirical "regular solution" form[7]:

$$\begin{aligned}\mu_3(X_u,T)&=G_3{}^0+RT\ln X_u+1.57R(1-X_u)^2,\\ \mu_4(X_l,T)&=G_4{}^0+RT\ln(1-X_l)+1.57RX_l{}^2.\end{aligned}\tag{5}$$

Substitution of Eqs. (5) into (1) now give simultaneous equations from which the X_l and X_u can be determined to give the phase separation line. We do not give the complete expressions here but only their limiting form at low temperatures, i.e., when terms involving $(1-X_u)^2$ $X_l{}^2$, $\ln X_u$, $\ln(1-X_l)$, etc., can be neglected and $V_u=V_3{}^0$, $V_l=V_4{}^0$, $G_3{}^0=-L_3{}^0$, $G_4{}^0=-L_4{}^0$, where $L_3{}^0$ and $L_4{}^0$ are the latent hearts of the pure isotopes at the absolute zero. The limiting forms are

$$\begin{aligned}X_l&=\{2(2\pi m_3{}^*kT)^{\frac{3}{2}}V_4{}^0/Nh^3\}\\ &\qquad\times\exp[(NE_3-L_3{}^0)/RT],\\ (1-X_u)&=\{(2\pi m_4{}^*kT)^{\frac{3}{2}}V_3{}^0/Nh^3\}\\ &\qquad\times\exp[(NE_4-L_4{}^0)/RT].\end{aligned}\tag{6}$$

It will be noticed that unless the expressions in square brackets turn out to be zero, the temperature variation of the concentration along the separation line is predicted to be exponential at sufficiently low temperatures.

The value of the binding energy per mole for He^4 in He^3, NE_4 in the Zharkov and Silin theory, has been determined by de Bruyn Ouboter *et al.*[1] from specific heat measurements on a 95.4% He^3 mixture. Their value is 53.6 j/mole so that $(NE_4-L_4{}^0)/R=(53.6-59.50)/R=-0.71$°K. The effective mass, $m_4{}^*$, has not yet been measured experimentally; its value has therefore been determined at 5.3 m_4 by fitting the more exact form of the theory [using Eqs. (1), (3), and (5)] with the experimental values of X_l and X_u at 0.5°K.

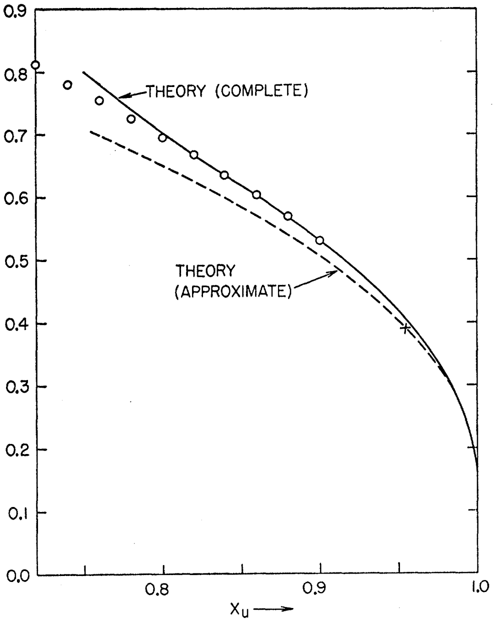

FIG. 1. The phase separation line for He^3-rich mixtures. ○, Roberts and Sydoriak[6]; +, de Bruyn Ouboter *et al.*[1]; – – –, ———, theory.

With the above values for the constants we obtain the full curve shown in Fig. 1 for the phase separation line in He^3 rich mixtures. The broken line represents the limiting form of the theory, valid when $T\rightarrow 0$, given by Eq. (6), or numerically,

$$(1-X_u)=1.13T^{\frac{3}{2}}\exp[-0.71\text{°K}/T].$$

It is indistinguishable from the more exact form below 0.3°K. Some predicted values of the He^4 concentration in the upper phase at very low temperatures are: 0.2°K, 0.3%; 0.1°K, 0.003%; 0.05°K, 10^{-6}%. However, these figures depend critically on the small difference between NE_4 and $L_4{}^0$, and it is possible that E_4 depends appreciably on concentration (see below). On the other hand, it is encouraging that the agreement between experiment and theory as shown in Fig. 1 is quite good over a substantial range of He^4 concentration.

It is much more difficult to make any definite predictions for the left-hand corner of the phase diagram, i.e., for small concentrations of He^3 in He^4, owing to the small value of $(NE_3-L_3{}^0)$. The experimental values of NE_3 obtained by de Bruyn Ouboter *et al.* between 0.6°K and 1°K range from 23.8 j/mole at $X=0.1$ to 21.8 j/mole at $X=0.02$, which may be compared with $L_3{}^0=21.2$ j/mole. Using these data, de Bruyn Ouboter *et al.* have calculated a separation curve for temperatures above 0.3°K which is consistent with extrapolation of the known experimental curve. But a value of NE_3, larger than $L_3{}^0$ and independent of concentration, would imply from Eq. (6) that, $T\rightarrow 0$, X_l does not tend to zero but actually begins to increase with decreasing temperature. This means that sufficiently dilute solu-

---

[6] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **118**, 901 (1960).

[7] R. de Bruyn Ouboter, J. J. M. Beenakker, and K. W. Taconis, Physica **25**, 1162 (1959); A. K. Sreedhar and J. G. Daunt, Phys. Rev. **117**, 891 (1960).

tions of He^3 in He^4 would not separate into two phases at 0°K. In mixtures containing enough He^3 for phase separation to occur, the equilibrium concentration of He^3 in the lower He^4-rich phase at 0°K would then be determined by higher order terms in the free energies which have not been included in (6).

On the other hand, the experimental values of NE_3 appear to vary approximately linearly with concentration and are not inconsistent with the hypothesis that $NE_3 \rightarrow L_3^0$ as $X \rightarrow 0$. This hypothesis removes any unusual behavior from the separation line near absolute zero, but it is difficult to accept from another viewpoint: It implies that the binding energy of He^3 does not depend at all on whether its neighbors are He^3 or He^4.

ACKNOWLEDGMENTS

We wish to thank the National Science Foundation and The Research Corporation for their generous support, and Dr. A. M. Sessler for interesting discussions.

PHYSICAL REVIEW VOLUME 124, NUMBER 3 NOVEMBER 1, 1961

Dissipation in Quantum Mechanics. The Harmonic Oscillator. II

I. R. SENITZKY
U. S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey

(Received May 4, 1961)

The development of a quantum-mechanical formalism for systems with dissipation that was presented in an earlier article, and intended mainly for application to the electromagnetic field in a cavity, is extended. The problem of the harmonic oscillator with dissipation is shown to be the same as that of a harmonic oscillator coupled to a thermal reservoir, and the need of the formalism to contain the appropriate statistical mechanics is discussed. The derivation of relationships which permit the calculation of all moments of the oscillator coordinate and momentum provides the necessary extension of the theory. The formal resemblance of the completed theory to that of classical Brownian motion, some differences due to quantum mechanics, and the fact that certain fundamental relationships which are assumed in the latter are derived in the present analysis, are pointed out. The application of the theory is illustrated by the consideration of three problems: the proof of Ott's formula, and the derivation of both the probability density and energy distribution of the oscillator in equilibrium with a thermal reservoir.

INTRODUCTION

IN the first article on the present subject[1] (hereafter referred to as I), a quantum-mechanical theory of the harmonic oscillator with dissipation was developed. The motivation behind this theory was its application to the electromagnetic radiation field in a resonant cavity, and for this purpose, the analysis was carried sufficiently far. Recently, the theory has been applied to an entirely different subject,[2] and some questions arose which were not treated in I. In view of this and, possibly, other applications not yet envisaged, it is the purpose of present article to extend the above theory.

The results of I will be summarized for the sake of intelligibility. They will be presented in a modified notation, the modification having no other significance than the simplification of the appearance of analytic expressions.

The new notation is defined, essentially, by the statement that the part of the total Hamiltonian which refers to the harmonic oscillator alone (and not to the coupling between it and the loss mechanism or possible driving mechanism) is given by

$$H_{\text{osc}} = \tfrac{1}{2}\hbar\omega(q^2 + p^2), \tag{1}$$

with

$$[q,p] = i. \tag{2}$$

We will refer to q and p as coordinate and momentum, respectively. Comparing Eq. (1) with the analogous expression for the electromagnetic field of a mode of (angular) frequency ω in a resonant cavity, or with that for a mechanical oscillator, we can obtain immediately expressions for the electric and magnetic field strengths or for the coordinate and momentum of the mechanical harmonic oscillator.[3] The loss of the oscillator is described, as in I, by the constant β which is the reciprocal relaxation time of the oscillator. [Energy other than thermal or zero-point energy decays as $\exp(-\beta t)$. For the resonant cavity, $\beta = \omega/Q$, Q being the quality factor.] It is assumed throughout that

$$\beta/\omega \ll 1. \tag{3}$$

The results of I are contained, essentially, in the following two relationships:

---

[1] I. R. Senitzky, Phys. Rev. **119**, 670 (1960).

[2] T. J. Krieger, Phys. Rev. **121**, 1388 (1961).

[3] The electromagnetic field of a cavity mode is given by $\mathbf{E} = -(4\pi\hbar\omega)^{\frac{1}{2}} p(t)\mathbf{u}(\mathbf{r})$, $\mathbf{H} = (4\pi c^2\hbar/\omega)^{\frac{1}{2}} q(t)\nabla\times\mathbf{u}(\mathbf{r})$, where $\mathbf{u}(\mathbf{r})$ is a normalized function describing the spatial dependence of the cavity field. The coordinate and momentum of a mechanical oscillator of mass m are given by $q_m = (\hbar/m\omega)^{\frac{1}{2}} q$, $p_m = (\hbar\omega m)^{\frac{1}{2}} p$.