

Thermodynamic theory of thin-film ^3He - ^4He solutions*

Marvin Chester

Physics Department, University of California, Los Angeles, California 90024

Jean-Pierre Laheurte and Jean-Pierre Romagnan

Laboratoire de Physique de la Matière Condensée, [†] Université de Nice, Parc Valrose 06034, Nice, France

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Expectations are presented with regard to the concentration profile and the extent of superfluidity in thin films of ^3He - ^4He in a van der Waals field. A thermodynamic method of analysis is outlined which, although treating a somewhat idealized configuration, is amenable to experimental confirmation. The connection between this analysis and experiment is discussed in detail.

I. INTRODUCTION

In recent years, a plethora of data¹⁻³ has been gathered on adsorbed films of pure ^4He . Interest in this system obtains because superfluid properties are significantly altered in constrained geometries. The thin-film constrained geometry has been somewhat favored because it is particularly amenable to analysis. Analyses^{4,5} which idealize the system as uniformly flat and of uniform thickness d have been remarkably fruitful, although this treatment has been a matter of controversy.⁶

Recently, interest has been developing for similar systems of the ^3He - ^4He isotopic mixture.^{7,8} Close to a boundary wall, the superfluid properties of the mixture differ from those in the bulk.⁹⁻¹² This effect is presumed to arise from the van der Waals attraction which atoms feel in the neighborhood of a solid boundary. This same attraction is the postulated cause of some of the observed nucleation effects of the normal fluid-superfluid phase separation at low temperatures.⁹ Motivated by the foregoing observations, we wish to offer here an analysis of the thermodynamic effects produced by the van der Waals potential upon a ^3He - ^4He mixture of finite extent. We consider a thin-film system of thickness d reasonably greater than a few monolayers. However, the analysis carries over, of course, to bulk systems, by allowing d to approach infinity. Because we are primarily concerned here with the van der Waals force in systems with relatively large d , we neglect the surface-tension effects at the free surface. These produce a preferential adsorption of ^3He at the free surface.¹³⁻¹⁶ Hence our estimates of the concentration profile will be slightly in error over about one atomic distance near the free surface. We defer further discussion of this effect until enough empirical data are available to

evaluate the general accuracy of the present offering.

In what follows then, our objects are (i) to present the thermodynamic theory by which thin-film ^3He - ^4He mixtures in a van der Waals force field may be understood and analyzed. (ii) To deduce from this foundation a number of practical consequences. Examples of these are a generalized analog to the Frenkel-Halsey-Hill isotherm; the connection between film thickness (generally not measured) and measurable parameters; the concentrations, pressure, and density profiles in the film, and the extent of superfluidity in the film. (iii) To outline some simple data-analysis procedures by which experimental results may be used, to validate (or invalidate) the applicability of the theory presented. (iv) To provide the basis by which information on the more fundamental physical processes governing the mixture thin-film system may be extracted. The raw experimental data on such systems are an amalgam of fundamental thermodynamic expectations in combination with microscopic information on superfluidity in a constrained geometry. To extract the latter a firm grasp of the former is essential. Hence, the present theory is offered in order to realize the potential utility of thin-film experiments in studying superfluid characteristic length effects in ^3He - ^4He mixtures.

II. EXPERIMENTAL CONFIGURATION

A picture of the experimental configuration is schematized in Fig. 1. A gas mixture, at a concentration c of ^3He in a ^3He - ^4He mixture, fills an experimental chamber at temperature T . The measured pressure of the gas mixture in this chamber is p . Necessarily, every accessible surface inside the experimental chamber is covered with an adsorbed film of components condensed from the

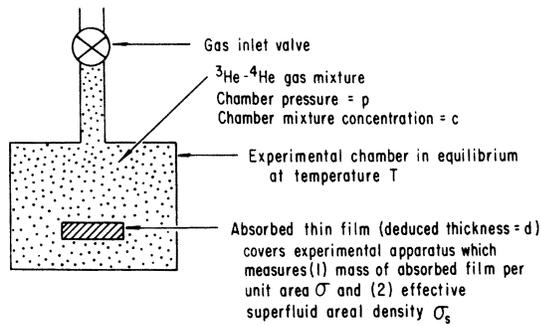
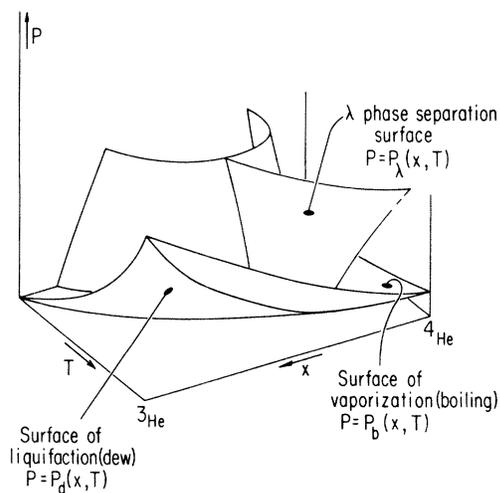


FIG. 1. Idealized experimental configuration.

mixture of chamber gases. Via the technique of third sound, the quartz-crystal microbalance, the superfluid gyroscope, or other method, the mass per unit area of superfluid in the film, σ_s , and perhaps σ , the total adsorbed mass per unit area, can be measured experimentally. In what follows we wish to establish a connection between these measured variables and quantities of interest, such as the film thickness d and its composition. The link is found via the measured characteristics of the bulk system, as exhibited in the phase separation surfaces in P - x - T phase space. (See Fig. 2.)

III. THEORETICAL FOUNDATION

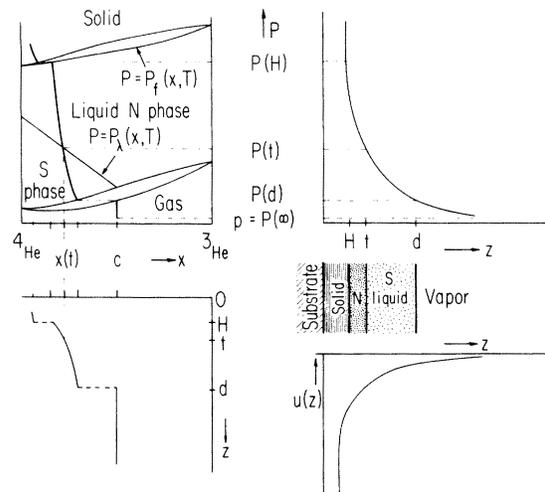
As has been done with some success in the pure- ^4He case,^{4,5} we treat the film, even on the microscopic scale of several atom layers, as if it were quite macroscopic. That is, we apply the principles of thermodynamics to the thin-film system as if it were a macroscopic continuum covering an

FIG. 2. Schematic view of the gas-liquid and normal-superfluid phase separation surfaces in x - T - P space.

ideally flat substrate (cf. Fig. 3). This procedure incorporates two admittedly tenuous assumptions. The first is that the interfaces are ideally flat. And the second is that one can describe the state of the film in terms of local thermodynamic variables even on a length scale comparable to the average interparticle spacing. We proceed in the face of these idealizations on the following bases: (i) This hypothesis has proved relatively successful in the pure- ^4He case. (ii) This is a basic hypothesis underlying the Frenkel-Halsey-Hill¹⁷ isotherm behavior. These isotherms have been empirically verified and employed to analyze a large variety of applicable systems.^{3, 18} (iii) We will suggest some experimental tests which may be used to verify the conclusions from our idealized film continuum hypothesis. The concurrence of theory and experiment must constitute the ultimate justification for this model.

Proceeding under the foregoing postulate then, we understand the phenomenon of physical adsorption as follows. Matter condenses on a substrate due to the attractive force of the van der Waals potential, $u(z)$. This potential arises from the dipole-dipole interaction between the atoms in the substrate and those introduced into the experimental chamber. A conceivable form for $u(z)$ is illustrated in Fig. 3 where, of course, z is the distance between the substrate and some point above it—either in the adsorbate or in the gas.

A fundamental principle of thermodynamics applies when particles of a system are interchangeable among its phases. That is, the "total"

FIG. 3. Schematic views of the pressure, van der Waals energy, and concentration profiles in a ^3He - ^4He film demonstrating the relationship between these quantities. The x - P diagram represents a cut along the plane $T = \text{const} > 0.9^\circ\text{K}$ through the surfaces representing phase equilibrium in x - T - P space.

chemical potential of each component is independent of position. In the presence of an external field the total chemical potential is the sum of two terms. The first is the "bulk" potential, as obtained from a bulk phase diagram (cf. Figs. 2 and 3). The second is the external potential energy per particle due to the force field in which the system finds itself. In the present case, because the two components are isotopes of the same chemical species, we presume that the van der Waals potential per particle $u(z)$ is the same for each component. Following standard procedure the bulk chemical potential for the species ν ($\nu=3$ or 4) is related to the bulk Gibbs free energy, $G(T, P, N_3, N_4)$ for the system by

$$\mu_3(x, T, P) = \left(\frac{\partial G}{\partial N_3} \right)_{T, P, N_4}, \quad (1)$$

where, of course, the analogous equation obtains also for $\nu=4$. x represents the concentration of ^3He in the system.

Representing the total chemical potentials by starred quantities and the bulk ones—obtained via phase diagrams—as unstarred, the principle of thermodynamic equilibrium enumerated above leads to

$$\mu_3^* = \mu_3(x(z), T, P(z)) + u(z), \quad (2)$$

where μ_3^* is independent of z , and

$$\mu_4^* = \mu_4(x(z), T, P(z)) + u(z), \quad (3)$$

where μ_4^* is also independent of z .

These two equations determine the position variation of the concentration x and the pressure P , i.e., P and x must change in such a way as to keep the total chemical potentials constant with position z . This notion, together with the constancy of T (also an equilibrium condition) and the continuity of pressure, yields the relevant parameters of interest.

With regard to the van der Waals potential $u(z)$, we note that customarily it is assumed to be of the form

$$u(z) = -K\theta(D_0/z)^3, \quad (4)$$

where the value D_0 is traditionally taken as 3.6 \AA . This length corresponds to the mean distance between ^4He atoms under normal vapor pressure conditions. Hence, D_0 is used as the yardstick by which statistical layers of pure ^4He are measured. The parameter θ is a constant characterizing the substrate-helium intraction strength. Employing the value $D_0 = 3.6 \text{ \AA}$, the θ found in the literature^{3, 19, 20} ranges from about 15 to 90 °K. The exponent 3 seems to provide an adequate fit to data in many cases, but values up to 4 and down to 2 have been discussed, as well as a continuous

variation of the exponent with z .^{19, 20}

To proceed further, we take note that some important and accessible physical quantities²¹⁻²⁴ are directly related to the derivatives of μ_ν . In particular the volume per atom v_ν for each of the species ($\nu=3, 4$) is given by

$$v_\nu = \left(\frac{\partial \mu_\nu}{\partial P} \right)_{x, T}, \quad \nu = 3, 4. \quad (5)$$

We define another accessible parameter γ by

$$\gamma(x, T, P) \equiv \frac{x}{KT} \left(\frac{\partial \mu_3}{\partial x} \right)_{T, P}. \quad (6)$$

This same dimensionless function is also necessarily connected to μ_4 by virtue of the Gibbs-Duhem relation connecting μ_4 to μ_3 . Hence, we have

$$\left(\frac{\partial \mu_4}{\partial x} \right)_{T, P} = -\frac{x}{1-x} \left(\frac{\partial \mu_3}{\partial x} \right)_{T, P} = -\frac{KT}{1-x} \gamma(x, T, P). \quad (7)$$

In the important cases of an ideal-gas mixture and for dilute liquid solutions of any kind ($|x - \frac{1}{2}| \approx \frac{1}{2}$), γ is just simply unity.

We now may write (2) and (3) in the more useful differential form as

$$0 = (KT/x)\gamma dx + v_3 dP + du, \quad (8)$$

$$0 = -[KT/(1-x)]\gamma dx + v_4 dP + du. \quad (9)$$

With these two equations plus a detailed knowledge of $u(z)$ and the dependence of the v_ν and γ upon x , T , and P , the concentration profile $x(z)$ and pressure profile $P(z)$ are, in principle, exactly obtainable. The problem is reduced to the simultaneous solution of (8) and (9).

Before proceeding to these solutions, we may obtain some instructive and interesting general results by examining the three differential statements obtained by eliminating dP , then dx , and finally du between (8) and (9). To do so profitably it is expedient to define the volume difference Δv and a "mean" volume per atom v . The volume difference is

$$\Delta v \equiv v_3 - v_4. \quad (10)$$

For the present system, Δv is always non-negative. The mean volume is

$$v \equiv xv_3 + (1-x)v_4. \quad (11)$$

This quantity always lies between v_3 and v_4 , and hence remains within 15% of the average of v_3 and v_4 for the present system.

In terms of v and Δv eliminating dP from (8) and (9) we find that

$$d \ln [x/(1-x)] = (\Delta v/v)(1/\gamma KT) du. \quad (12)$$

This constitutes a direct and quantitative statement

of the often quoted notion^{9, 10, 12} that the concentration gradient near a bounding wall is due to the difference in size between ^3He and ^4He atoms in the presence of a van der Waals force field. Because Δv is always positive, Eq. (12) assures us that the concentration of ^4He increases toward the wall in the attractive van der Waals force field.

Eliminating dx from (8) and (9), we arrive at the statement

$$v dP = - du. \quad (13)$$

This equation details directly how the pressure varies with position. The pressure rises as one proceeds inward toward the wall where the van der Waals potential energy plunges downward.

Finally, eliminating du from (8) and (9), we find the curve in x - P space ($T = \text{const}$) describing the variation of concentration with pressure within a particular phase of the system

$$d \ln [x/(1-x)] = - (\Delta v / \gamma K T) dP. \quad (14)$$

Within the context of the hypotheses underlying this thermodynamic treatment, Eqs. (12)–(14), like (8) and (9), are exact. We now proceed to deduce some of the consequences of the foregoing employing approximations where necessary.

IV. THICKNESS d OF A ^3He - ^4He FILM

In the region $d < z < \infty$ the mixture is a gas. We will assume the gas to be an ideal one. For an ideal gas $\gamma = 1$ and

$$v_3 = v_4 = v = KT/P, \quad d < z < \infty. \quad (15)$$

As discussed in Sec. II, we presume that the chamber gas pressure p and concentration are known. Hence, we want to obtain everything in terms of

$$p = P(z = \infty), \quad (16)$$

and

$$c = x(z = \infty). \quad (17)$$

By virtue of (12) and (13), we immediately see that in the vapor

$$x(z) = c = \text{const}, \quad d < z < \infty, \quad (18)$$

and

$$P(z) = p e^{-u(z)/KT}, \quad d < z < \infty. \quad (19)$$

Now at the position $z = d$, the gas phase is in contact with the liquid phase of the system. Hence, the thermodynamic variables x , T , and P at the position $z = d$ must have values which correspond to some point on the liquefaction surface (or dew surface) in x - T - P space. Let us denote the equation representing the dew surface (surface of liquefaction) by

$$P = P_d(x, T). \quad (20)$$

Thus, the statement that the film liquid meets the gas mixture at the position $z = d$ becomes

$$P(z = d) = P_d(c, T). \quad (21)$$

This is also the statement that the thickness of the film is to be called d . Combining (18), (19), and (20) with $z = d$, Eq. (21) assumes the more useful form

$$u(d) = KT \ln [p/P_d(c, T)]. \quad (22)$$

Because the surface (20) is obtained through measurements on the bulk system, the function $P_d(x, T)$ is quite accessible in the literature.²⁵ Furthermore, $u(z)$ also has a long history of accessibility. This was discussed around Eq. (4). Hence, Eq. (22) may be utilized to estimate the thickness d of the film from measurements of c , p , and T . If one utilizes the inverse cube law for u , as indicated in (4), Eq. (22) is just the analog of the Frenkel-Halsey-Hill isotherm.^{17, 18} The single-component counterpart of (22) has the vapor pressure in place of $P_d(c, T)$. For a two-component system, the liquefaction surface $P_d(c, T)$ must be employed. Of course, in the limits $c = 0$ or $c = 1$, Eq. (22) reduces properly to the known single-component result, as it must.

Equation (22) may be utilized to test the validity of the concepts employed in this exposition. If one could measure the film thickness d directly as a function of p , c , and T , then Eq. (22) predicts that d is a universal function of these parameters when combined into the form $[p/P_d(c, T)]^T$, i.e., Eq. (22) predicts that if one plots the function $KT \ln [p/P_d(c, T)]$ vs d , the myriad of experimental points for all temperatures, concentrations, and pressures should lie on a single universal curve. By contrast, if one uses p as the ordinate, no universal curve should result. The experimental points would scatter over the plane. In the case of the single-component ^4He system, this test has proven quite positive.⁵ The experimental points for pure ^4He have been shown to coalesce into a universal curve when the proper ordinate and abscissa were chosen. The appearance of such a universal curve for the mixture would constitute an indication of the validity of the theory presented here.

V. CONCENTRATION PROFILE AND PHASE BOUNDARIES WITHIN THE FILM

At the film surface $z = d$, the concentration must suffer a discontinuity. The change in phase plus the continuity of pressure and temperature across this boundary demand this. Let the equation yielding the locus of all points x , T , and P on the sur-

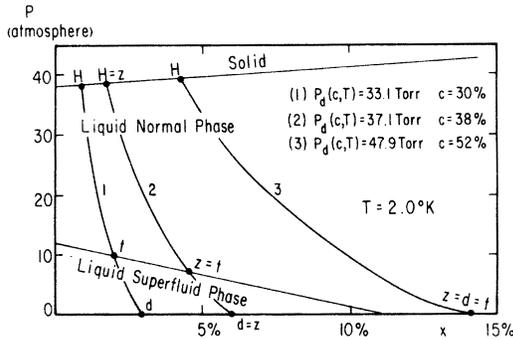


FIG. 4. Concentration of ^3He vs pressure inside the film liquid. The curves are plotted for the three conditions listed.

face of vaporization (boiling) be

$$P = P_b(x, T). \quad (23)$$

Then, the concentration on the liquid side of the boundary $x(z = d -)$ must be the one which satisfies the relation

$$P_d(c, T) = P_b(x(d -), T). \quad (24)$$

As is evident in Fig. 3, the concentration $x(d -)$ is easily obtained from plots of the dew and boiling curves in x - P space at the fixed temperature of interest.

Having obtained $x(d -)$ through (24), and knowing $P(d)$ by virtue of (21), we proceed further into the film via Eqs. (13) and (14). Depending upon the relative value of x , one may employ either v_4 or v_3 for v . For example, in the three quantitative cases illustrated in Fig. 4 where, in the film, x is always small, the value $v \approx v_4(0, T, P)$ was employed. In general, however, the pressure at any position $z < d$ is simply determined by the integrated form of (13):

$$\int_{P_d(c, T)}^{P(z)} v dp = u(d) - u(z). \quad (25)$$

The integral of Eq. (14) yields the concentration profile upon being given the pressure profile from (25). More directly, it yields the curve of concentration vs pressure at constant fixed T . Again, to integrate (14), some approximations will generally be necessary if a computer computation is to be avoided. With regard to γ , we take note here that information on this function is obtainable via the variation of v_3 and v_4 with concentration. In particular, a simple thermodynamic Maxwell relation yields

$$\frac{\partial \gamma}{\partial P} = \frac{x}{KT} \frac{\partial v_3}{\partial x} = - \frac{1-x}{KT} \frac{\partial v_4}{\partial x}. \quad (26)$$

We immediately deduce that if the atomic volumes

do not vary greatly with concentration, γ does not stray too far from its ideal value of unity. In any case, if γ is taken as unity within the film, then the theory is only applicable for the two dilute cases ($x \approx 0$ or 1). With regard to Δv , the "dilute approximation" is also employed. For example, in Fig. 4, the values of v_3 and v_4 at concentration $x \approx 0$ were used.^{23, 24} Subjected to the approximations appropriate to the situation, we see that

$$\ln \frac{x}{1-x} = \ln \frac{x(d-)}{1-x(d-)} - \frac{1}{KT} \int_{P_d(c, T)}^P \frac{\Delta v}{\gamma} dP. \quad (27)$$

In Fig. 4, three curves derived from (27) are plotted. All of these obtain at the temperature $T = 2.0^\circ\text{K}$. The curves correspond to the cases $x(d-) = 3, 6,$ and 14% . Also plotted in Fig. 4 is a cut, at constant T , of the λ surface^{26, 27}

$$P = P_\lambda(x, T), \quad (28)$$

and a similar cut of the freezing surface²⁷

$$P = P_f(x, T). \quad (29)$$

The former divides the superfluid and normal fluid phases of the liquid mixture. The latter, together with the surface of melting, divides the solid phase from the liquid phase of the mixture. Of course, as shown in Fig. 2, the λ surface opens into two sheets below $T = 0.87^\circ\text{K}$. This produces a concentration discontinuity at low temperatures analogous to those which occur between gas and liquid, and between liquid and solid. Figure 4 (and Fig. 3) illustrate the significance of these surfaces.

If we denote by $z = t$ that physical boundary inside the film at which the normal phase and the superfluid phase are in contact, it is clear that we must have

$$P(t) = P_\lambda(x(t), T). \quad (30)$$

This states that the intersections marked "t" in Fig. 4 correspond to the position $z = t$ in the film. Alternatively, the simultaneous solution of (28) and (27) determines the critical values of x and P , where the phase change takes place. Inserting this value of P into (25) determines the position $z = t$. As an illustrative example, if we employ $\theta = 27^\circ\text{K}$ in Eq. (4), and we inspect the case where d is sufficiently large ($u(d) \approx 0$), we find for the positions t in Fig. 4 that t (d is large) = 7.6 and 8.2 \AA , and $t = d$. In the last case, all of the liquid part of the film is in the normal state. There is no superfluid region, even though the concentration of ^4He in this film exceeds 95% near the solid boundary.

In the cases where two distinct liquid phases are present, we note the unexpected result that the normal phase is on the substrate side, and the superfluid phase is on the free surface side of the

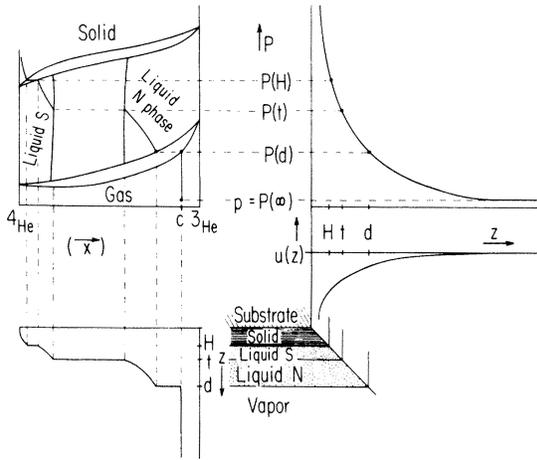


FIG. 5. Schematic views of the pressure, van der Waals potential, and concentration profiles in a ^3He - ^4He film demonstrating the relationship between these quantities. The P - x diagram represents a cut along the plane $T = \text{const} < 0.8^\circ\text{K}$ through the surfaces representing phase equilibrium in x - T - P space.

liquid. This is unexpected because the concentration of ^4He is largest on the substrate side and smallest on the free-surface side. The resolution to this paradox derives from the rapid pressure rise as one proceeds in toward the substrate. Although the concentration of ^4He rises in this direction, it does not rise enough to overcome the pressure effect. Hence, we have the superfluid region of the film where in fact the concentration of ^4He is lowest, and the normal region where it is highest quite contrary to a priori expectations.

Just as the key length t is estimated via (30), the solid undercoat thickness H may be estimated via analogous reasoning. This leads to

$$P(H) = P_f(x(H), T). \quad (31)$$

Here the intersection of the x - P curve from (27) with the freezing curve is the determining factor in finding $x(H)$ and $P(H)$. Having located these, one finds H itself from (25) just as in the case of t . Again for the case of large d [$u(d) \approx 0$] and $\theta = 27^\circ\text{K}$ in Eq. (4), we find for the three cases illustrated in Fig. 4 that $H = 4.9, 4.9,$ and 4.8 \AA .

Figure 5 illustrates the situation at a lower temperature (below $T = 0.8^\circ\text{K}$, for example) where it is the ^4He that is dilute in the gas ($c \approx 1$). We see that it is again possible to have two liquid phases in the film. However, in this regime, the superfluid phase is on the substrate side, and the normal fluid phase is on the free-surface side. This contrasts with the higher temperature case where this configuration is reversed. Furthermore, although the concentration x spans the entire gamut of values between dilute ^4He ($x \approx 1$) to dilute ^3He

($x \approx 0$), the configuration may be accessible to an analytical solution employing only the dilute approximations. This obtains because x jumps discontinuously through the region $x \approx \frac{1}{2}$ from dilute values on one side to dilute values on the other. The analytical part of the calculation need only be applied at the two extremes. Although x must, in principle, pass through values for which $\gamma \neq 1$, it does so by a discontinuous leap. This obviates the necessity of treating this regime analytically.

Figure 6 constitutes a quantitative example for the low-temperature regime. The temperature here is 0.4°K . The pressure vs concentration is presented for two cases of dilute ^4He . These are for $x(d^-) = 97\%$ and $x(d^-) = 99.5\%$. Again these curves derive from Eq. (27), while the phase-separation curves and the freezing curve come from Refs. 22 and 28. The horizontal dashed line corresponds to the concentration discontinuity and to the pressure at the position $z = t$. For the case of a relatively thick film [$u(d) \approx 0$], and for $\theta = 27^\circ\text{K}$, the values of t and H are exhibited in the figure.

VI. SUMMARY AND CONCLUSION

In the foregoing we have outlined the thermodynamic theory for a ^3He - ^4He mixture of finite extent in the presence of a van der Waals force field. A number of experimentally accessible properties of this system have been enumerated, and a general method for interpreting data on ^3He - ^4He adsorbed thin films has been outlined with examples to illustrate the technique.

The entire analysis is based on an idealization of the system. Each local part of the film has been characterized by its macroscopic thermodynamic bulk properties. Therefore, the present offering details the expectations for an "ideal"

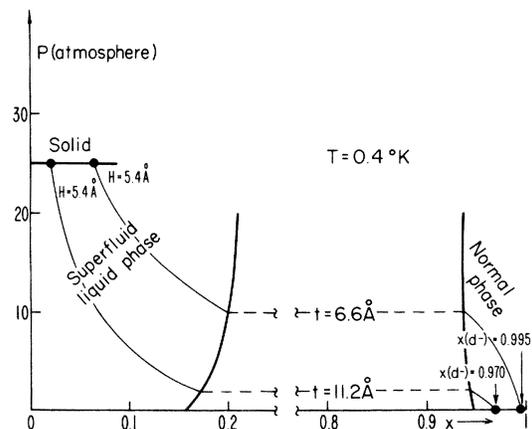


FIG. 6. Concentration of ^3He vs pressure inside the liquid film under the two conditions listed.

system. If recent experience with adsorbed films of pure ^4He is any guide, this ideal behavior will account, in large measure, for the experimental observations. However, as in the pure case, we anticipate deviations from this ideal behavior in the matter of, say, the superfluid content σ_s . Hence, as for the pure- ^4He case, it is expedient to have the expectations for the ideal case available, in order to recognize the existence and extent of the deviations from them. It is precisely these departures from ideal which carry the in-

teresting microscopic information on such matters as the healing length in superfluidity.

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