

Classification  
 Physics Abstracts  
 7.460 — 7.700

## NUCLEATION OF SUPERFLUID TRANSITIONS IN LIQUID HELIUM MIXTURES

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(Reçu le 19 juillet 1976, accepté le 9 septembre 1976)

**Résumé.** — Les transitions superfluides dans les mélanges d'hélium liquide sont étudiées dans un modèle de continuum en tenant compte des gradients de concentration et de pression induits par l'existence de parois. La localisation des nouvelles phases et leurs évolutions sont obtenues en considérant les propriétés massives. Nos mesures de temps de relaxation nous fournissent la température de formation de film superfluide  $T_{\text{as}}$  pour différents mélanges au-dessus de 0,9 K. Ces résultats ainsi que ceux d'autres expérimentateurs sont analysés dans ce modèle. Il apparaît une longueur caractéristique d'observation de la phase superfluide qui croît avec la température et très fortement vers 1,1 (K).

**Abstract.** — Superfluid transitions in liquid helium mixtures are studied in a continuum model including concentration and pressure gradients induced by the walls. The localization and growth of the new phases are obtained using the bulk phase properties. Relaxation times have been measured and they yield the *onset* superfluid temperature  $T_{\text{as}}$  for several mixtures above 0.9 (K). These results and others found in the literature are analysed in the model. We find a characteristic *onset* length which increases with the temperature.

**1. Introduction.** — The study of superfluid and phase separation transitions in liquid helium mixtures has been the subject of numerous theoretical and experimental investigations. It is quite remarkable that helium experiments have been crucial in improving our general understanding of transitions (as for instance in the determination of critical exponents [1]). The essential features of the transitions in helium are schematically shown in figure 1a. Below 0.87 K the mixtures are not stable for all  $^3\text{He}$  concentrations,  $x$ , and temperatures  $T$ , so that one finds phase separation surfaces. At  $T = 0$  K pure  $^3\text{He}$  liquid coexists with a dilute  $^4\text{He}$  liquid mixture. Rich  $^4\text{He}$  mixtures show a superfluid behaviour which is not observed with dilute  $^4\text{He}$  mixtures. The border between the normal and superfluid phase is a line in the  $T, x$  plane. The transition temperature  $T_{\lambda}$  decreases when both the  $^3\text{He}$  concentration  $x$  and the pressure  $P$  increase. In addition the domain of instability is smaller in the  $T, x$  plane when  $P$  increases.

Different determinations of the transition temperatures have shown that, depending on the experimental method used, great care in the interpretation is required.  $^4\text{He}$  is subject to a preferential adsorption [2] near the walls, and a superfluid film creeps along the walls while the bulk mixture remains not superfluid. This was quite obvious in the case of phase separation observations [2] in dilute  $^4\text{He}$  mixtures. More recently [3], the superfluid transition in helium mixtures has been studied in a vycor glass superleak over a large range of temperature and concentration. These observations strongly indicate that the concentration inhomogeneity also affects the lambda transition. The measured onset temperature of wall film superfluidity is then larger than the bulk transition temperature for a given concentration (Fig. 1b).

It appears, therefore, that a good understanding of the transition nucleation both for the phase separation and the lambda transition is required to explain

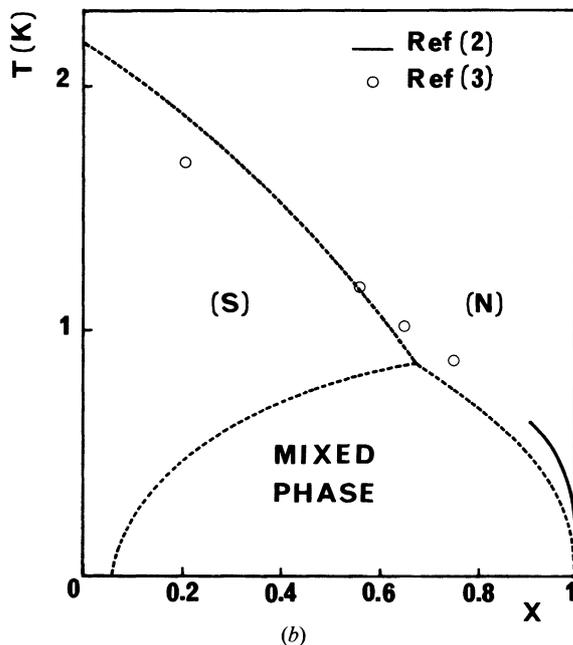
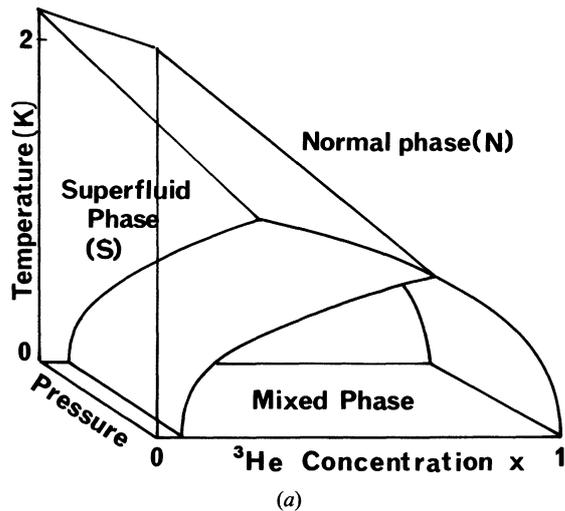


FIG. 1. — *a*) Schematic view of the phase diagram of  $^3\text{He}$ - $^4\text{He}$  mixtures in  $T$ - $x$ - $P$  space. *b*) Phase diagram under saturated vapour pressure (dashed lines) and experimental onset superfluid temperatures from ref. [2] and [3].

many experimental observations in bulk mixtures. In this paper we present a model which describes quantitatively the growth of the new phase and explains and predicts all observations connected with the spatial dependence of the transition.

The validity of the model and the role of dimensionality are checked by comparison with previous experimental results [2, 3], and our measurements in a range of temperature and concentration not yet fully explored.

In section 2 we present calculations based on a continuum model, which using the bulk properties of the phases give the localization of any superfluid transition in the mixture and describe the growth of the new phase. In section 3 we present experimental results of relaxations times in the liquid which give

the superfluid film formation temperature  $T_{\lambda S}$  vs.  $x$  between 0.9 (K) and 1.1 (K). These results and other measurements found in the literature are compared with the model in section 4. The existence of a healing length in the new superfluid phase which nucleates in bulk helium mixtures is discussed.

**2. Nucleation of transitions.** — We consider mixtures with two kinds of boundaries. One with the walls of any solid material in contact with the liquid, the other is the free surface. As is well known [4], in such a case, the new phase will preferably nucleate at one boundary. Since it costs less work to build interfaces with the new phase at the boundary. However, the situation is complicated because both the pressure and concentration are not uniform in the mixture. The locations of the new phase will therefore depend upon competitive effects coming from the pressure and concentration gradients that must be analysed.

The first step is, of course, to know the concentration and pressure profiles in the liquid mixture. Recent results [5] of calculations in the frame of a continuum model give these profiles. In this model there are two important assumptions : firstly, that the interfaces are ideally flat; and secondly, that local thermodynamic variables are used even on a length scale comparable to the average interparticle spacing.

Such a continuum model has already proven to be quite successful in describing  $^4\text{He}$  films [6], which gives a great confidence in using it for the study of liquid mixtures. Comparison of experimental results with theoretical predictions is, of course, the ultimate test. In the model the  $^3\text{He}$  preferential adsorption, at the free surface, in the very first liquid layer is not included. The concentration profile is therefore obtained in all the liquid, except at the free surface. This is sufficient in view of our goal, which is to describe the nucleation and superfluid phase growth. It is essentially governed by the concentration inhomogeneity induced by a Van der Waals interaction with the walls.

Writing the equilibrium conditions in the liquid [5], two equations are obtained from which the concentration and pressure profiles can be deduced :

$$v \, dP = - \, du \quad (1)$$

$$d \ln \left( \frac{x}{1-x} \right) = - \frac{\Delta v}{\gamma k T} \, dP \quad (2)$$

where the mean volume  $v$  is related to the volume of a  $^3\text{He}$  atom  $v_3$  and  $^4\text{He}$  atom  $v_4$  :

$$v = xv_3 + (1-x)v_4 \quad (3)$$

with

$$\Delta v = v_3 - v_4 . \quad (4)$$

The pressure is  $P$ , while  $u$  is the Van der Waals

interaction energy with walls; the parameter  $\gamma$  is defined as :

$$\gamma(x, T, P) = \frac{x}{kT} \left( \frac{\partial \mu_3}{\partial x} \right)_{T,P} \quad (5)$$

$\mu_3$  being the  $^3\text{He}$  chemical potential.

The value of  $\gamma$  is 1 in the case of dilute solutions or ideal mixtures. No exact expression for  $\gamma$  is known for the whole range of  $T$  and  $x$ . From experimental results [7] on helium mixtures which give an empirical relation for  $\mu_3$ , we obtain :

$$\gamma \simeq 1 - 3.08 (1 - x) \frac{x}{T}. \quad (6)$$

This is only an approximate relation, which has the advantage of allowing one to obtain the profile determinations for all mixtures and temperatures by integrating eqs. (1) and (2).

Such calculations have already been done for dilute solutions at high and low temperatures [5]. We have extended these calculations for all concentrations and temperatures using eq. (6). Our results are presented in a  $P(x)$  plot (Fig. 2). We know that any  $P$  value is related to the distance  $z$  from the walls through (1), which gives the spatial profiles. The concentration at the liquid-gas boundary,  $x_d$  is obtained for  $P$  equal to the saturated vapour pressure ( $P \simeq 0$ ).

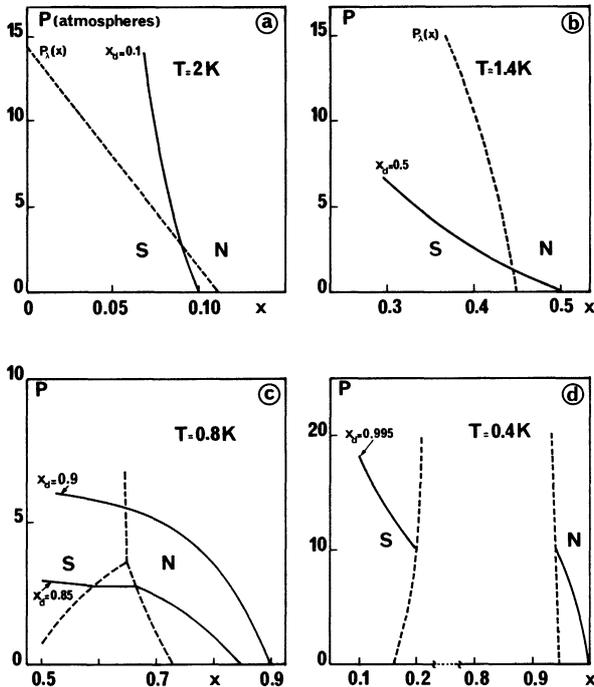


FIG. 2. — Profile of the  $^3\text{He}$  concentration  $x$  versus pressure (full lines) at four different temperatures. The dashed lines represent the cross-section of the phase diagram (Fig. 1a) at constant temperature. a)  $T = 2 \text{ K}$  : the superfluid phase grows from the free surface. b)  $T = 1.4 \text{ K}$  : the superfluid phase grows from the wall. c)  $T = 0.8 \text{ K}$  according to the starting concentration  $x_D$  one can observe lambda transition ( $x_D = 0.90$ ) or phase separation ( $x_D = 0.85$ ). In both cases the superfluid phase appears near the wall. d)  $T = 0.4 \text{ K}$  : the phase separation occurs near the wall.

Obviously in the case of thick film mixture  $x_d$  is nothing but the average (or initial) concentration.

In the frame of our continuum model for describing the new phase growth, we expect the two phases (normal and superfluid) to be in contact at a distance  $z = e$  from the walls when

$$\mu_{iN}[P(e), x_N(e), T] = \mu_{iS}[P(e), x_S(e), T] \quad (7)$$

the chemical potentials of each isotope ( $i = 3, 4$ ) are equal in the normal, N, and superfluid, S, phases.

Rigorously, we should take into account the finite dimension of the new phase [8]. In the approach of Ginzburg-Pitaevskii [9] the superfluid component can be represented by an order parameter,  $\psi$  which satisfies the differential equation

$$\frac{\partial^2 \psi_S}{\partial \eta^2} + \psi_S(\eta) - \psi_S^3(\eta) = 0 \quad (8)$$

with  $\eta = z/l$  and  $l$  is a healing length function of temperature. In addition to (8) we need two boundary conditions for  $\psi_S$ . One, fairly well accepted condition, is that  $\psi_S = 0$  at the liquid-solid interface. The other one is not so obvious. For the case of a pure  $^4\text{He}$  film the value of  $\psi_S$  at the liquid-gas interface is already subject to controversy [10-11] and leads to minimal healing length values varying from 0 to 0.25 atomic layer. In the mixture it is probable that the order parameter at the interface between the normal and superfluid phase is not zero. The two phases are very close in nature and we believe that a good comparison could be made with a superconducting S-normal N double layer where it is known [12] that the order parameter is  $\neq 0$  in the N material. The characteristic length of variation of the order parameter in normal helium should be very short  $\simeq$  atomic layer [13]. When considering the superfluid transition there is probably no interface between the normal and superfluid phase. The concentration changes continuously, and this is probably also true for the order parameter.

It does not seem obvious, therefore, to include, in a simple way, the finite geometry effects in this calculation. In consequence we are going to describe the phases as bulk in what follows. By comparison of the experimental results with theoretical predictions we should then be able to show if the introduction of dimensional effects is effectively required.

In bulk systems the conditions for transitions are measured and well known [14-15]. They give for the phase separation  $P_{PS}(x, T)$  while for the superfluid transition we have  $P_\lambda(x, T)$ .

For a given temperature  $T$  and initial concentration  $x_d$ , we get the superfluid transition when [14] :

$$P_\lambda(x, T) = P(x, x_d, T) \quad (9)$$

and the phase separation for [15]

$$P_{PS}(x, T) = P(x, x_d, T). \quad (10)$$

The distance  $e$  at which the interface between phases is located is obtained using the value of  $P$  (solution of (9) or (10)) in eq. (1).  $P_\lambda(x, T)$  is also presented in figure 2 and we observe that the intersection point with the profile curve gives the solution of (9).

At high temperatures (Fig. 2a,  $T \simeq 2$  K), the slope of the profile curve is large with respect to  $P_\lambda(x, T)$ . The only possible intersection point is obtained for  $P \simeq 0$ . The nucleation of the superfluid phase therefore starts at the lowest pressure, i.e. far away from the walls at the free surface. The superfluid phase grows from the free surface. The rise of the  $^4\text{He}$  concentration near the walls does not overcome the pressure increase which reduces the transition temperature. In this case we do not expect a discrepancy between bulk transition and superfluid film observation. At a lower temperature, as shown in figure 2b, the rise of  $^4\text{He}$  concentration overcomes the pressure effect so that the intersection point first appears at the highest pressure. We then expect the superfluid phase to grow from the liquid-solid boundary. Obviously in this range, bulk and first observations of the transitions should be different.

In the third domain figure 2c,

$$0.87 \text{ (K)} < T < 0.73 \text{ (K)},$$

we can observe the phase separation and the superfluid transition. Here again the superfluid phase nucleates at the walls. From our calculation we predict that in this range it is possible to observe a superfluid phase at the walls without separation (intersection with  $P_\lambda(x, T)$ ). Reducing the temperature for the same mixture the profile curve will then cut  $P_{\text{PS}}(x, T)$ . The superfluid phase rich in  $^4\text{He}$ , being located near the walls.

Finally, at low temperatures (Fig. 2d),  $T \lesssim 0.73$  K, the  $P_\lambda(x, T)$  curve disappears. The new superfluid phase still grows from the walls and our calculations give us the localization of the new superfluid phase. The growth of this phase with temperature is described, finding at each temperature the intersection point between the profile curve and one of the equilibrium curves. We obtain a value of  $P$  solution, which reported in (1) gives  $e$ . We are then able to plot  $e(T)$ . A typical example for the growth of the superfluid phase is given in figure 3.

**3. Experimental results.** — We present in this section experimental observations which can be explained by superfluid film formation between 0.9 (K) and 1.1 (K). They are complementary to the measurements carried out at lower temperatures [2] and through a vycor superleak [3]. In the experimental chamber (Fig. 4) the liquid mixture is used as the dielectric of two capacitors. The distance between the plates is  $\lesssim 0.1$  mm. These capacitors are part of two tunnel diode oscillators. The frequency measurement is related to the dielectric constant of the

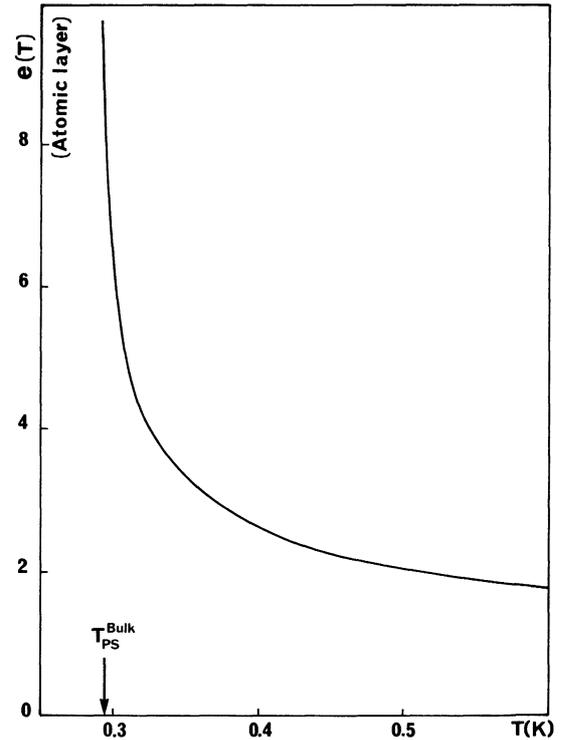


FIG. 3. — Temperature variation of the superfluid phase thickness  $e(T)$  for a liquid  $^3\text{He}$ - $^4\text{He}$  mixture ( $x_D = 0.98$ ).

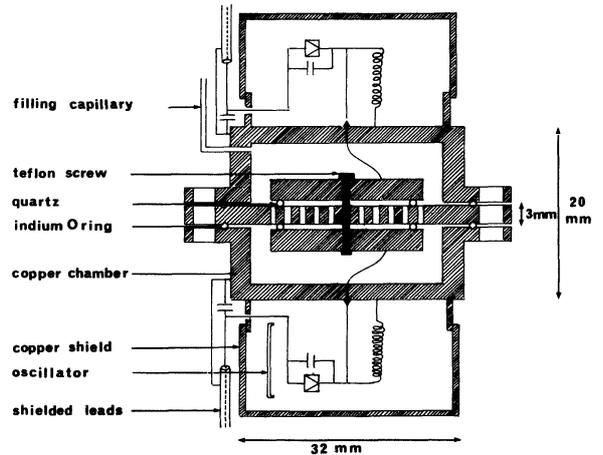


FIG. 4. — Mixture chamber.

liquid. We are able to detect a frequency variation of  $10^{-7}$  or what is equivalent a concentration change  $\simeq 2 \times 10^{-5}$ .

Our observations were made during a study of the osmotic compressibility near the tricritical point <sup>(1)</sup>. For a given mixture, we measure both a thermal relaxation time  $\tau_T$  and the time  $\tau_{\text{eff}}$  required to reach a density equilibrium between the capacitor plates, as the temperature of the chamber is reduced. The thermal relaxation time  $\tau_T$  is obtained through the temperature measurements of the copper experimental chamber, while  $\tau_{\text{eff}}$ , identical for the two capacitors, is obtained measuring the dielectric constant.  $\tau_{\text{eff}}$

<sup>(1)</sup> DANDACHE, H., BRIGGS, A. and PAPOULAR, M., to be published.

is function of the thermal relaxation time in the liquid and the mass diffusion relaxation time. Typical observations at high  $T$  are presented in figure 5a. Clearly,  $\tau_{\text{eff}} \gg \tau_T$  and the increase of  $\varepsilon$  comes from the molar volume decrease with temperature.

For the same mixture and at a lower temperature we observe a transitory effect during a time comparable to  $\tau_T$ . The dielectric constant  $\varepsilon$  first decreases following which the expected behaviour of  $\varepsilon$  is obtained (Fig. 5b). This transitory effect is reproducible and is always observed below a temperature  $T_{\lambda S}$  depending on  $x$ . We notice that  $T_{\lambda S}$  is higher than the bulk lambda temperature of the mixture. We propose the following explanation for this effect. In reducing the temperature, it is of course first the copper chamber and liquid layers in good thermal contact with the chamber which are cooled down. The liquid layers between the capacitor plates are therefore probably a cold point in the liquid. During this time interval there is a temperature gradient in the liquid. If the liquid is normal there is no transient effect. Otherwise, we detect, through the reduction of  $\varepsilon$ , a  $^4\text{He}$  superfluid film transfer towards the warmest liquid layers [16]. We observe variations  $\simeq 2 \times 10^{-5}$  to  $10^{-4}$  of the  $^4\text{He}$  concentration between the plates. As soon as the temperature gradient disappears the process of mass diffusion governs the behaviour of  $\varepsilon$ . From these experiments we obtain an estimation of  $T_{\lambda S}$  which is the temperature at which the transient effect appears.

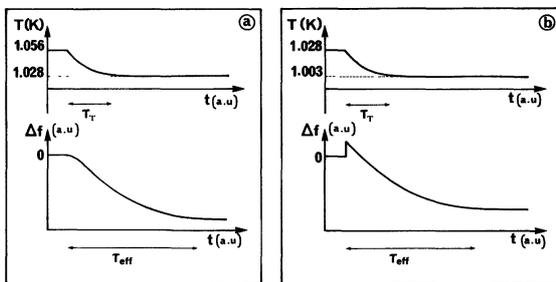


FIG. 5. — Typical observations in our experiment of the temperature and the frequency variations versus time. The thermal relaxation time  $\tau_T \simeq 1$  min. a) When reducing the temperature, the liquid density reaches its new equilibrium value in a time  $\tau_{\text{eff}} \simeq 30$  min. The frequency variation  $\Delta f$  reflects the molar volume decrease. b) At lower temperature we observe a transitory effect (reflecting a dielectric constant decrease) during a time comparable to  $\tau_T$ . Then the expected behaviour is obtained.

**4. Discussion.** — Our experimental results  $T_{\lambda S}$  are plotted figure 6. On the same diagram are given the experimental points obtained with a vycor superleak [3]. All the observed transition temperatures are consistent and fit on a smooth curve that comes very close to the bulk  $T_\lambda$  curve around 1.1 (K). As previously noticed by Gearhart and Zimmerman [3], we find that this line joins reasonably well the superfluid film line obtained at lower temperature [2]. These experimental results,  $T_{\lambda S}(x_d)$ , and previous measurements [2] of the superfluid film detection  $T_{SS}$

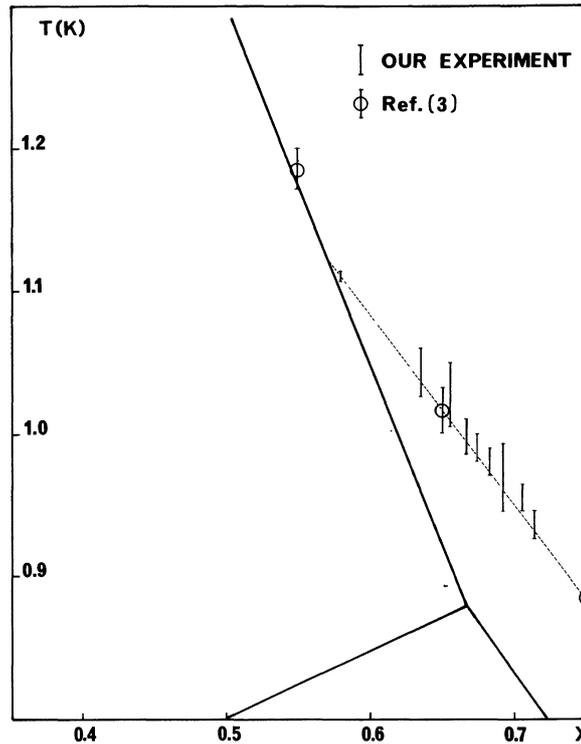


FIG. 6. — Measurements of the superfluid onset temperatures  $T_{\lambda S}$  versus  $^3\text{He}$  concentration  $x$ .

at lower temperatures have been analysed in our model (for  $T_{SS}(x_d)$  we use the maximum onset temperature values). For each couple  $T_{\lambda S}$ ,  $x_d$  or  $T_{SS}$ ,  $x_d$  we find the value of  $P$  solution of eq. (9) or (10). Then with the help of eq. (1) we infer the distance  $e$  of the interface between the normal and superfluid phase. This is related to a length for the onset of superfluidity  $l_0$  :

$$e = d_s + l_0$$

where  $d_s$ , the solid helium thickness can be obtained from eq. (1) knowing the melting pressure of the mixture. Its order of magnitude is 1.5 atomic layers, with the standard definition of atomic layers in helium of 3.6 Å. In our evaluation we used as Van der Waals interaction  $u(z) = -27(\text{K})/Z^3$  [17], with  $Z$  in atomic layers.

This is summarized in figure 7, which plots the superfluid onset lengths  $e$  vs.  $T$ . It is clear that all these measurements give onset lengths which are consistent. The error bars for the onset temperatures also give the uncertainties in the onset length. All these results fit on a smooth curve, figure 7. However, it should be kept in mind that the initial concentrations  $x_d$  are not the same for the different temperatures.

It is then clear that for low temperatures and large  $x_d$ ,  $l_0$  is small, and increases at higher temperatures and lower  $x_d$ . We know that the superfluid onset length is always larger than the healing length [18], but for pure  $^4\text{He}$  the temperature dependence of the healing and onset length are similar [17].

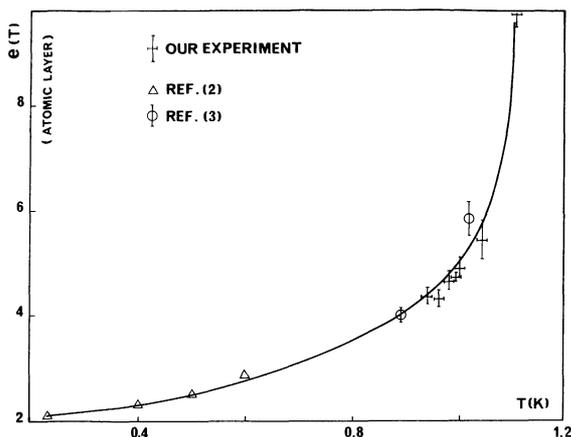


FIG. 7. — Superfluid film thickness at the detection calculated in our model from our measurements and experimental results of references [2] and [3].

We therefore expect that for our mixtures the behaviour of the healing length is also well described by the curve given in figure 7. From this we deduce that the healing length will certainly be different from zero at least in the high temperature range. It is then obvious that dimensional effects or surface excitations are going to play a role in the nucleation of the superfluid phase even in bulk mixtures.

The study of film mixtures should of course be useful for understanding the relative roles of  $x$  and  $T$  on the healing length. In films the concentration is fixed and the temperature dependence of the healing length obtained, changing the film thickness  $d$ . However, one should note that the boundary condition for the

order parameter at the normal superfluid or gas-superfluid interface remains a crucial parameter. We suggest that in any theory, one should use it as an adjustable parameter, as was done for instance in the theory of normal-superconducting double layers [19].

In conclusion we have shown in this work that calculations of helium mixtures, using a continuum model and bulk phase properties give the localization of the superfluid phase nucleation and describe its growth. The localization depends upon competitive effects due to the increase of pressure and reduction of  $^3\text{He}$  concentration near the walls. The superfluid phase appears near the free surface at high temperature when the pressure effect is dominant. At low temperatures the situation is reversed and the superfluid phase nucleates near the walls. In this last case the spatial dependence of the transition is experimentally observed. We also predict that between 0.87 (K) and  $\simeq 0.73$  (K) there will be successively a superfluid transition and a phase separation near the walls for the same mixture. Our experimental measurements of relaxation time confirm the spatial dependence of the superfluid transition in bulk mixtures previously observed in a vycor glass superleak. They show that dimensionality effects should probably be introduced at high temperature for a better description of the superfluid phase nucleation process.

**Acknowledgments.** — We are grateful to Prof. E. Guyon for helpful comments.

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