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Interface fluctuations and stratification in $^3$He-$^4$He mixture films

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Résumé. — Considérant l’état stratifié induit par le champ d’interaction de Van der Waals avec le substrat nous développons un modèle phénoménologique des films minces de mélanges avec une description en terme de multicoches. L’introduction des fluctuations dans ce système multicouches nous permet de décrire les excitations de densité, de respiration et capillaires des interfaces. Ces fluctuations désstabilisent la structure stratifiée dans un domaine d’épaisseur de films qui s’aminscit et tend vers zéro lorsque la température est réduite. Ce comportement est observé dans nos mesures de $^3$e son de films de mélange $^3$He-$^4$He, qui étudient à la fois les dépendances en épaisseur et température de la transition stratifiée-homogène. L’accord quantitatif entre la théorie et nos expériences est obtenu en améliorant la description de champ moyen par l’introduction d’un argument dynamique qui tient compte des fluctuations de courte longueur d’onde.

Abstract. — Starting from the stratified state induced by the substrate Van der Waals field, we develop a phenomenological model for « thin » mixture films in terms of a multilayer description. Introducing fluctuations in this multilayer system allows us to describe interface excitations which are found to destabilize the stratified structure in a film thickness range which shrinks to zero as the temperature is reduced. This behaviour is observed in our third sound measurements of $^3$He-$^4$He mixture films which study both the thickness and temperature dependence of the stratification-homogeneous transition. A quantitative agreement between the theory and our experiments is achieved by improving the mean field description with the introduction of a dynamical argument involving short wavelength fluctuations.

1. Introduction.

Stratification is the usual manifestation of a phase separation in a two component system. The existence of an external field will break the spatial symmetry and induce the stratification. For instance bulk liquid mixtures of helium show a phase separation below a tricritical temperature $T_t = 0.88$ K. This gives a stratification in the mixture chamber because of the mass difference between the two isotopes.

Gravity plays the major role so that the denser $^4$He rich phase is located at the bottom while the lighter phase rich in $^3$He is at the top. The phase separation is not observable for mixtures of $^3$He concentration less than $6.4 \%$ down to 0 K. Considering mixture films of sufficient thickness we also expect to observe a phase separation. However, in this case, gravity will not be the dominant field. It is rather the Van der Waals interaction with walls which will be responsible for the spatial separation. This leads to the preferential adsorption of $^4$He near the walls and $^3$He at the free surface [1-3].

This preferential adsorption is also related to the mass difference between the helium isotopes through the zero point motion leading to a volume occupied by a $^4$He atom smaller than for a $^3$He atom. The minimization of the Van der Waals interaction potential of the mixture with the substrate will lead to the localization of the largest possible number of atoms near the substrate, resulting in a preferentially adsorbed $^4$He rich phase near the wall. Conversely at the free surface, the atoms are less bounded which favours the adsorption of a smaller number of atoms, i.e. of a $^3$He rich phase. The preferential adsorption thus induces a natural stratification of the mixture films. This stratification should however be affected by the film dimension. Reducing the film thickness, which means going from a 3D to 2D regime, we expect that the influence of interfaces and (or) density fluctuations becomes important.

The existence of a stratification transition in $^3$He-$^4$He films has been observed recently [1]. The study of third sound velocity at $T = 0.4$ K clearly shows two types of behaviour. When the $^4$He thickness is
larger than 16.2 Å, which roughly corresponds to 4.5 atomic layers of 3.6 Å size, the film mixture appears stratified with pure or almost pure 4He near the walls. When the 3He thickness is less than 4.5 atomic layers, the third sound velocity suggests homogeneous behaviour. The stratification transition is found to be a smooth function of the 4He thickness. The description of such a transition in terms of interface fluctuation was already proposed in a letter [1]. The goal of this work is both to develop this model and extend the measurements to lower temperatures. The second section which describes the model considers carefully the various contributions to interface fluctuations in thin films and discusses their influence on the stability of a stratified system. Section 3 presents our experimental results which are compared to the model predictions. Finally the last section summarizes our results and include some concluding remarks.

2. Theory of the stratification transition.

2.1 INTRODUCTION. — In order to describe the stratification transition, we propose to consider the influence of the interface fluctuations; such an effect is usually neglected except near critical points or for phenomena involving a delocalization of the interface (roughening or wetting transition).

In our quasi-two-dimensional systems, the importance of the interface fluctuations stems from the finiteness of the film thickness which, as we shall see, is not much larger than the magnitude of these interface fluctuations. In a stratified 4He-3He film, one can identify essentially three interfaces, namely the substrate-4He, 4He-3He and 3He-gas interfaces.

The first one is much more rigid than the other two even when considering the solid 4He atomic layer adsorbed on the substrate. As a consequence, its fluctuations should be negligible compared to those of the fluid interfaces.

Up to now, we have considered the fluctuations in the broadest possible sense. The question arises whether it is possible to identify and classify different modes of fluctuations for the fluid 4He-3He and 3He-gas interfaces. Since our film thicknesses range from ~ 3 to 8 atomic layers, we are interested in describing the structure of the interfaces down to the atomic level. At this scale an interface has an intrinsic width in the order parameter profile of the order of the correlation length of the system. The next step consists in identifying the disturbances around the mean-field profile. By going beyond the classical approximation, one finds essentially three different types of excitations [4]:

— A spectrum of gapless modes arising from the breaking of translational invariance which corresponds on the microscopic level to the intuitive notion of capillary wave like excitations.

— A spectrum of modes whose gap goes to zero at the (tri) critical point and which correspond to squeezing the interface (a kind of breathing mode).

— The continuum states in the third band which are completely similar to that of a homogeneous bulk system.

We can develop a feeling for the importance of these excitations by computing the r.m.s. displacement of a single interface within the usual capillarity — wave fluctuations analysis [5] which considers the first type of excitations. One obtains:

$$\langle z^2 \rangle \sim \frac{k_B T}{\alpha} \log \frac{L}{l}$$

where $\alpha$ is the surface tension, $k_B$ the Boltzmann constant, $T$ the temperature, $L$ the typical size of the interface and $l$ a microscopic scale of the order of an atomic radius.

As an example, for a 4He gas interface at 0.4 K, we get $\langle z^2 \rangle^{1/2} \approx 6$ Å for $L = 0.2$ μm. This result suggests that if for large film thicknesses $d$ or low temperature such that $d \gg \langle z^2 \rangle^{1/2}$, the interface undergoes free fluctuations, while for thin films or higher temperature ($d \sim \langle z^2 \rangle^{1/2}$), its wandering becomes constrained.

However, this description of the interface fluctuations which clearly decouples the capillary and breathing modes should be taken with care for the systems of such low dimensions we are studying.

For example, we can expect intuitively that because of the smallness of the distances between the 3He-gas, the 4He-3He interfaces and the substrate in the stratified case, the capillary excitations (rippons) are coupled to the thickness fluctuations of these two interfaces (breathing). A precise treatment of these couplings can be undertaken within the « classical » description of interfaces but does not seem worthwhile to develop considering the discrete nature of the system (atomic scale) and the quantum nature of the problem (discretization of the position of the 3He atoms...).

2.2 MODEL FOR THE STRATIFIED FILM. — Therefore we propose here to proceed by dwelling more specifically on the choice of variables which could provide the simplest and fullest description of a distortion from the stratified regime taken as a reference. Since the transition from a stratified to a homogeneous state corresponds to a change of the profile of the 3He concentration (and alternatively of 4He concentration) in the direction perpendicular to the substrate, it seems natural to keep a description which is invariant with respect to translations parallel to the substrate. In the spirit of the work of Kjellander and Marcelja [7] on inhomogeneous fluids near a wall we describe the inhomogeneous system by subdividing it into $M$ layers of thickness $d/M$ which lie parallel to the substrate surface. In the stratified regime, each layer is homogeneous and characterized by a certain value of the 3He concentration. For slow enough spatial disturbances, the state of the system can be characterized unambiguously by considering the surfaces of
equal mean $^3$He concentrations. The mean concentration can of course only be defined in a coarse grained sense. Since all scales are small, the coarse-graining should be replaced by a time average. This averaging is meaningful if the time scale of the probe (third sound) is large compared to typical relaxation times as is the case in our experiment. Such a surface can be viewed as the deformed state of the layer defined above at the same given concentration. In this way, fluctuations around the stratified regime can be viewed as displacement fluctuations for each layer of given $^3$He concentration. This description assumes that the topology is that of parallel layers, a hypothesis which excludes the possibility of inclusion of droplets etc. This assumption is however not restrictive if as indicated above a time average is taken and if small enough disturbances are considered. Let us denote $u_i(r_z)$ the displacement of the $i$th layer where $r_z$ is a two-dimensional vector parallel to the substrate.

The notation may be simplified by substituting for the discrete index $i$, the continuous variable $z = i.a$ with $a$ being an atomic scale:

$$ u_i(r_z) \rightarrow u(r_z, z) = u(r). \quad (2) $$

Let us now determine the free energy $g$ per unit volume of the perturbed (stratified) system as a function of the derivatives of $u(r)$.

The contributions to the free energy are essentially of two types:

A first term describes the cost in free energy associated with an increase of the surface of a given layer. In analogy with usual surfaces this contribution should be similar to a surface tension energy (namely an energy increase proportional to the surface increase) with a surface tension here of the order of $a/d$ where $a$ is the sum of the surface tension of the $^3$He-gas and $^3$He-$^4$He interfaces in the stratified regime. In other cases, $a$ depends of course of the precise concentration profile and as we shall see (Fig. 9) it can be measured indirectly up to a multiplicative constant. We assume here for convenience that the subdivision into layers is made in such a way that the surface tension constant of each layer is roughly the same.

The second term takes into account the interactions between different layers and has three different physical origins. Each layer is defined by its position but its width may change as a result of these interactions. A first contribution comes from the disturbance around the mean field profile of the stratified regime. The associated intrinsic rigidity depends on the microscopic interactions between $^3$He and $^4$He atoms and the substrate. As a consequence, this effect leads to an energy contribution $\frac{1}{2} B_{int} \left( \frac{\partial u}{\partial z} \right)^2$ where $B$ is a constant independent of the thickness of the film.

A second effect stems from the steric hindrance felt by the different fluctuating layers which are not allowed to cross either each other or the substrate. When the deviation $\langle u^2 \rangle$ of a given layer is less than but still on the order of the thickness $d$, numerous "collisions" or "contacts" may appear between adjacent layers or between a layer and the substrate. As analyzed elsewhere [8], this leads to the appearance of an effective steric repulsive interaction of entropic origin which takes the same form as that of the intrinsic contribution.

Finally, we must take into account the influence of the substrate Van der Waals attraction which also leads to an effective repulsion between the layers. To see this, let us consider a local increase $+\delta \rho$ of the $^3$He concentration at the altitude $z$ which is balanced by a decrease $-\delta \rho$ at an altitude $z - \Delta z$. Within our multilayer picture, this fluctuation corresponds to a deformation of the layers as depicted in figure 1a. Alternatively, if $\delta \rho$ is negative, we obtain the deformation shown on figure 1b. Therefore, we can describe these types of fluctuations by a kind of extension-compression mode (which corresponds of course to the breathing mode in the single well-defined interface case).

The energy associated with such a deformation can be estimated by considering the schematic example of a way to realize a given $^3$He concentration fluctuation as shown on figure 2, corresponding to an interchange of an $^3$He and $^4$He atom. The Van der Waals energy of the configuration (a) is

$$ E_a = -\frac{\theta}{(d_4 - r_4)^3} + \frac{\theta}{(d_4 + r_4)} \quad (3) $$

where $\theta$ is the Van der Waals constant, $n$ the number of $^4$He atoms under the $^3$He atom, $r_4(r_3)$ respectively the radius of a $^4$He($^3$He) atom and $d_4 = 2 n r_4$ is the mean $^4$He thickness.

![Fig. 1. Schematic representation of a density perturbation in a film.](image_url)
Fig. 2. — Illustration of a way to achieve the density perturbations sketched in figure 1. Figure 2b is deduced from figure 2a by the exchange of a $^3$He atom by a $^4$He atom and conversely leading to an increase in Van der Waals energy for the total film computed in equations (6), (7).

The Van der Waals energy of the configuration (b) reads:

$$E_b = \frac{-\theta}{(d_4 + r_3 - 2r_4)^3} + \frac{-\theta}{(d_4 + 2r_3 - r_4)^3}. \quad (4)$$

The difference $E_b - E_a$ is:

$$\delta E = E_b - E_a \approx 6 \theta \frac{r_3 - r_4}{(2r_4)^3} = 6 \theta \frac{\Delta r}{d_4^3} \quad (5)$$

to first order in $\frac{\Delta r}{r_4} = \frac{r_3 - r_4}{r_4}$. This difference is positive corresponding to a decrease of the Van der Waals attraction.

Finally, we may write the layer interaction contribution to the free energy as a compression term

$$\frac{1}{2} B \left(\frac{\partial u}{\partial z}\right)^2$$

where $B$ is the effective elastic compression modulus embodying the repulsive effect of the intrinsic interface rigidity, the steric repulsion and the Van der Waals forces. However, for the small thicknesses we are considering, the Van der Waals contribution largely dominates [8] and we can therefore consider its effect only. Using the result (5) for the energy increase of a $^3$He-$^4$He atom exchange corresponding within our multilayer picture to

$$\frac{\partial u}{\partial z} \approx \frac{u_{i+1} - u_i}{l} \sim 2 \frac{\Delta r}{l}$$

we obtain the expression for $B$:

$$B \approx 3 \frac{\theta'}{d_4^3} \left(\frac{l^2}{\Delta r}\right) \quad \text{where} \quad \theta' = \frac{\theta}{l^3}. \quad (6)$$

Let us emphasize that this computation should be considered as giving only the thickness dependence and the order of magnitude of the effective compression modulus $B$.

We are reluctant to take the quantitative features of the model too seriously, for several reasons.

The $^3$He-$^4$He exchange mechanism depicted in figure 2 is only one among many other possibilities and a more correct treatment should average over all configurations.

Furthermore, we have not taken explicitly into account the finite width of the $^4$He-$^3$He interface which should somewhat delocalize the unperturbed position of an $^3$He atom. As a consequence, we propose to consider this effect by replacing the $1/d^4$ dependence in equation (6) by a $1/d^4$ embodying the idea that the $^4$He-$^3$He interface is fuzzy and delocalized up to the upper $^3$He-gas interface for small enough $^3$He coverage. Then

$$B \approx \frac{3 \theta'}{d_4^3} \left(\frac{l^2}{\Delta r}\right). \quad (7)$$

2.3 STABILITY OF THE STRATIFIED FILMS. — The analysis now proceeds as follows. The free energy density describing the distortion of the layers is given by:

$$\theta = \frac{1}{2} \left(\frac{\partial u}{\partial z}\right)^2 + \frac{\alpha}{2d} \left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial u}{\partial y}\right)^2 \right) \quad (8)$$

where $d$ is the order of the film thickness.

We could think of higher order terms like curvature contributions (as for smectic liquid crystals). However, these corrections are negligible as long as the « effective surface tension » $\alpha$ is not vanishing or more quantitatively when the typical length $(K/\alpha)^{1/2}$ is small compared to the concentration correlation length $\xi$ ($K$ is the curvature rigidity modulus).

An important remark is in order here:

As we shall see below, it is the existence of the compression term proportional to $(\partial u/\partial z)^2$ which is responsible for the existence of relatively large fluctuations. In the case of a single interface, the presence of an external field such as the Van der Waals attraction leads to a mass term (proportional to $u^2$) implying much reduced fluctuation amplitudes.

The physical interpretation of the $(\partial u/\partial z)^2$ term is the low cost in Van der Waals energy associated with parallel layer deformations. We thus end up with an expression (8) analogous to the first important contributions for a smectic liquid crystal with the exception that in this case the surface tension energy is replaced by a curvature contribution (involving second derivatives) [9].

The small continuous local displacement in the direction normal to the layers is written in the usual Fourier expansion

$$u(r) = \sum_q e^{i(q \cdot r + q \cdot r_0)} \cdot u_q \quad (9)$$

which with the equipartition theorem

$$\frac{1}{2} \left( Bq^2 \alpha + \frac{\alpha}{d} q^2 \right) \cdot u_q^2 \cdot L^2 \cdot d = \frac{1}{2} kT \quad (10)$$

yields
where \( q_{ll}(q_{L}) \) is the wave vector component parallel (perpendicular) to the interface normal axis.

In the limit of large interfaces, we replace the sum over the modes by an integral

\[
\sum_{q} \rightarrow \frac{L^2 d}{(2\pi)^3} \int_{0}^{\infty} dq_{ll} \int_{q_{1m}}^{q_{M}} \pi dq_{1m}^2
\]

where the cut-off values \( q_{\parallel M} \), \( q_{1M} \) and \( q_{1m} \) are given by

\[
q_{\parallel M} = \frac{\pi}{d} \quad q_{1M} = \frac{\pi}{L} \quad q_{1m} = \frac{\pi}{d}.
\]

Performing the double integration yields:

\[
\langle u^2 \rangle = \frac{kT}{8\pi \alpha Y_{M}} \times \left[-2Y_{M}\log Y_{M} + Y_{M}\log(Y_{M}^2 + 1) + 2\tan^{-1}Y_{M}\right]
\]

where we have taken the limit \( q_{1m} \rightarrow 0 (L \rightarrow \infty) \)

with \( Y_{M} = \left(\frac{d\mathcal{B}}{\alpha}\right)^{1/2} \left(\frac{1}{d}\right)^{5/2} \).

Defining \( d^* \) as

\[
d^* = \left(\frac{3\theta'}{\alpha \Delta r l}\right)^{1/5} l
\]

we get

\[
Y_{M} = \left(d^*/d\right)^{5/2}.
\]

As an order of magnitude we find that for numerical values related to \(^3\text{He}-^4\text{He}\) phase at the top layer (\( \alpha \approx 0.15 \ \text{erg/cm}^2; \ l \approx 3.6 \ \text{Å}; \ 2\Delta r \approx 0.1 \ 1; \ \theta' = 50 \ (K)); \ d^* = 4.6 \ \text{atomic layers}.

Let us now discuss the influence of these fluctuations characterized by the mean square amplitude \( \langle u^2 \rangle \) as given by equation (15) on the stratified-homogeneous transition.

Note that \( \langle u^2 \rangle^{1/2} \) which in our model has the meaning of a layer displacement should more accurately be taken as a typical length over which the \(^3\text{He}-^4\text{He}\) concentrations fluctuates.

The crucial idea is now to assume that if this typical length scale is of the order of the thickness of the film, then the behaviour will be homogeneous, whereas smaller values of \( \langle u^2 \rangle \) would lead to states not much disturbed compared to the « perfect » stratified regime taken as a reference. This is reminiscent of the Lindemann criterion for solid-liquid phase transitions [10]. Quantitatively, this amounts to assume the existence of a cross-over \( S \) separating two regimes:

stratified case \( \frac{\langle u^2 \rangle}{d^2} < S \) \hspace{1cm} (19)

homogeneous case \( \frac{\langle u^2 \rangle}{d^2} > S \) \hspace{1cm} (20)

We present in figure 3 the behaviour of the normalized relative square displacement

\[
\frac{\langle u^2 \rangle}{d^2} = \frac{8\pi \alpha d^*^2}{kT} = F
\]

as a function of \( d/d^* \) as obtained from equation (15). This curve shows the existence of three regimes:

— The strong field regime \( (d < d_1) \) for which the close proximity of the substrate and its corresponding Van der Waals interaction strongly hinders the fluctuation of the interfaces leading to a small \( \langle u^2 \rangle/d^2 \).

— The fluctuating regime \( (d_1 < d < d_2) \) corresponding to a thickness large enough for the Van der Waals interaction to be weaker and small enough for \( \langle u^2 \rangle \) to be comparable to \( d^2 \).

Fig. 3. — Behaviour of the normalized relative square displacement \( F = \frac{\langle u^2 \rangle}{d^2} \) as a function of \( d/d^* \). At a given temperature \( F \) must be compared to \( S \) and we can define three regimes. The model predicts a stratified behaviour for \( d < d_1 \) and \( d > d_2 \). In the thickness range \( d_1 < d < d_2 \) the magnitude of fluctuation becomes so large that one should observe homogeneous behaviour.

\[
\langle u^2 \rangle = \sum_{q} \langle u_q^2 \rangle \quad (11)
\]

\[
\sum_{q} \rightarrow \frac{kT}{L^2 d} \quad (12)
\]
The asymptotic regime \((d > d_2)\) for which the interfaces fluctuations become free and saturate whereas \(d\) becomes large.

The essential features predicted by this theory are simply illustrated in figure 3. At a given temperature \(T\) must be compared to \(S^* = S^0 + \frac{8 \pi a d^2}{k T}\). Of course if \(S^*\) is larger than the maximum value of \(F\) then the film will remain stratified for any thicknesses. Since \(S^*\) increases as \(T\) is reduced, at very low temperature all the films will be stratified. At a given temperature we can observe the following picture, when \(S^*\) being constant intersects the \(F\)-curve in two points as seen in figure 3. The model predicts that for thin films \(d < d_1\) the film is stratified. For a range of thicknesses \(d_1 < d < d_2\) the magnitude of fluctuations becomes so large that one should observe a homogeneous behaviour. Finally for thick films \(d > d_2\) the stratified structure of the film reappears.

3. Experimental results and discussion.

3.1 Experimental set up. — The goal of this work is to study the influence of temperature and coverage on the stratification in mixture films from third sound velocity measurements. In this paper we present results of our experiments using a time of flight technique on a glass plate with crushed glass as film reservoir, and using a third sound resonator filled with nuclepore filters.

The time of flight technique on a glass plate, already described elsewhere [11], is restricted to a narrow thickness range due to the occurrence of capillary condensation in the crushed glass [11]. In this respect nuclepore filter is a very interesting material which has been studied by Chen et al. [12]. Not only does it give a very large surface adsorption area but also it was shown [12] that capillary condensation occurs for coverage larger than 55 Å. It is then possible to study a very large thickness range without trouble.

Between two copper cylinders (1.2 cm i.d., 3.7 cm o.d. and 2.4 cm height) our resonance cavity is filled with 1,800 nuclepore filters adjusted to the cavity dimensions, and a plexiglass plate covers the top surface. The typical pore size is 0.2 µ and the total surface adsorption area is 57.7 m². The surface adsorption area and the thickness are estimated following the standard technique described previously [13]. From the ⁴He adsorption isotherm, we get a Van der Waals constant of the nuclepore material \(\theta = 50\) K (layers)³ [14].

On a nuclepore filter are evaporated the two strips of Ag and Al which are respectively the third sound emitter and the thermometer receiver. The fundamental resonance in the film is generated by driving continuously the emitter at a power of 1 µw and sweeping the frequency at a typical rate of 0.1 mHz/s. The receiver thermometer is operated in its superconducting transition region and its output voltage is detected by a lock-in amplifier. The measured resonance frequency is directly proportional to the third sound velocity \(C_3\). We check that the resonance frequency change with thickness for pure ⁴He agrees with the usual third sound velocity dependence. We also verify that a variation of heat power by a factor ten does not change our results.

3.2 Comparison with experimental results. Discussion. — The main trends predicted in the model of § 2 are indeed observed in our experiments.

We have measured at 0.4 K the third sound velocity \(C_3(d_3, d_4)\) in ³He-⁴He mixture films as a function of the ³He thickness for two different amounts of ⁴He, \(d_4 = 2.9\) (set A) and \(d_4 = 6.2\) layers (set C). Our experimental results are presented in figure 4 by plotting \(\frac{C_3^2(d_3, d_4)}{C_3^2(0)}\) as a function of \(d_3\), \(C_3^0\) being the third sound velocity of a pure ⁴He film with the same thickness \(d_4\).

The measured values of \(C_3^0\) are 22.1 m s⁻¹ for \(d_4 = 2.9\) and 8.7 m s⁻¹ for \(d_4 = 6.2\). For the lowest ⁴He coverage we have also included the results of our measurements obtained with a time-of-flight technique on a glass plate with crushed glass as film reservoir [11]. Obviously there is for this coverage good agreement between the third sound values obtained by the two different techniques. It was not possible to use this time-of-flight technique for the largest ⁴He coverage because of capillary condensation which occurs in the crushed glass. On the same figure are also presented two theoretical curves for \(\frac{C_3^2}{C_3^2(0)}\), with the assumption of either stratification or homogeneous behaviour.
In the case of stratification the calculation of Ellis et al. [15] gives, in the limit of complete separation, the relation

\[ \frac{C_3^2}{C_{30}^2} = 1 - \frac{n_3}{n_4} + \frac{n_3/n_4}{(1 + d_3/d_4)^2} \]  \hspace{1cm} (22)

where \( n_3 \) and \( n_4 \) are the number densities of pure \(^3\)He and \(^4\)He while \( d_3 \) and \( d_4 \) are the \(^3\)He and \(^4\)He coverages in the film expressed as thicknesses.

In the case of homogeneous behaviour we have

\[ \frac{C_3^2}{C_{30}^2} = \frac{\sigma_3(X, T)}{\sigma_3(0, T)} \frac{\rho(0) m(0)}{\rho(X) m(X)} \left[ \frac{d_3}{d_3 + d_4} \right]^4 \]  \hspace{1cm} (23)

where the mass \( m \) and density \( \rho \) depend on \(^3\)He molar concentration \( X \). The superfluid mass per unit area \( \sigma_3 \) is evaluated as in reference [11].

The theoretical curves presented in figure 4 are obtained from equations (22) and (23). It is clear that the experimental third-sound velocity is rather well described for the lowest \(^4\)He coverage (2.9 layers) by the assumption of homogeneous behaviour (Fig. 4). For the largest \(^4\)He coverage (6.2 layers) the experimental points suggest instead a stratification in the mixture film (Fig. 4).

The two sets of experiments characterize clearly the two kinds of behaviour, homogeneous or stratified. The next step is of course to study more accurately the change of regime with coverage. We therefore measure the third-sound velocity as a function of the \(^4\)He coverage \( d_4 \) at \( T = 0.4 \) K for two different \(^3\)He coverages (1 and 2 atomic layers).

The results are presented in figure 5 as \( C_3^2/C_{30}^2 \) with the theoretical curves still obtained from equations (22) and (23).

The third set of experiments (set B) shows the existence of a cross-over region, separating the stratified and homogeneous regimes, when \( d \) is varied from 4 atomic layers to 7 atomic layers.

These three sets of experiments at 0.4 K are grouped together in figure 6: they define three regions on the calculated curve presenting the behaviour of \( F \) as a function of \( d/d^* \). For \( d > 1.5 d^* \) the mixture film is stratified; we notice that our results are in good agreement with the experimental observations of McQueeney et al. [16] (see Fig. 6). Within our physical picture embodied in the model described in the preceding section, the homogeneous behaviour corresponds to thicknesses \( d_1 < d < d_2 \). In fact we observe a wide cross-over region between the homogeneous and stratified regimes indicating that the criterion (19), implying a sharp transition, should be considered only as an indication. Indeed, a sharp cross-over is the signature of a phase transition, a possibility which is not described by the model. The stratification transition appears rather as a finite size (thickness) effect leading to rounded behaviour.

The question arises whether it is possible to observe experimentally the other transition from homogeneous to stratified by crossing the other critical value \( d_1 \). In principle, this can be done in two ways, either by diminishing the film thickness below \( d_1(T) \) at fixed temperature or increased \( d_1(T) \) by lowering the temperature (i.e. increasing \( S^* \)) at fixed thickness. Considering the low value of \( d \) exhibiting a homogeneous behaviour, it is more convenient to proceed by decreasing the temperature.

One thus expects to observe a rapid increase of the third sound velocity as \( T \) is lowered below the transition temperature given by \( d_1(T^*) = d \).

Fig. 5. — Square of the relative third sound velocity at 0.4 K as a function of \(^4\)He coverage (set B). The full lines and the dashed lines represent respectively equation (22) and (23) for each \(^3\)He coverage. Experimental values are obtained by use of a resonator filled with nuclepore filters.

Fig. 6. — The three sets of experiments at 0.4 K are grouped together: set A (homogeneous behaviour), set C (stratified behaviour) and set B which shows the existence of a wide crossover region between the two regimes. The triangle on the right part of the continuous curve corresponds to the observation of Mac Queeney et al. [16].
This behaviour is indeed seen in our experiments using a time-of-flight technique. In figure 7 is given the variation of $C_3$ as a function of $T$ on films with constant amount of $^4\text{He}$ ($d_4 = 2.9$ layers) (set A) and with $^3\text{He}$ thicknesses ranging from $d_3 = 0$ to $d_3 = 2$ atomic layers. We interpret the steep increase of $C_3$ as the signature of a stratification.

Clearly, to test further the model of section 2, we need to compare more quantitatively with the experiments the expected thickness $d_3$ and temperature $T^*$ for which the stratification transitions occur. It is easy to convince oneself that the corresponding transition temperature $T^*$ (while showing the correct qualitative trend of decreasing with increasing amount of $^3\text{He}$), cannot be predicted quantitatively.

The occurrence of such a discrepancy is not surprising considering the rather crude level of our description and the mean field character of the model. The first assumption of small deformations (fluctuations) can be criticized especially in the proximity of the homogeneous-stratified transition.

Secondly, our theory is essentially mean field in the sense that the same compression elastic modulus $B$ has been taken for all mode disturbances with the usual consequence of overweighting the role of long-wavelength fluctuations. However, we think that as usual, the mean field approach predicts at least qualitatively the correct trend, namely the existence of three regimes.

Going beyond the mean field approach requires a more sophisticated description which is beyond the scope of this work.

However, at this stage, we may improve the mean field treatment with the following argument, already developed in a previous work [1]. It is natural to expect the treatment leading to equation (15) to be correct for small enough thicknesses for which the external Van der Waals field is strong. This case corresponds to the limit of large $Y_M$ in equation (15) and leads to the simple expression for $\langle u^2 \rangle/d^2$:

$$\frac{\langle u^2 \rangle}{d^2} \approx \frac{1}{5} \frac{kT}{\rho d^2} \left( \frac{d}{d^2} \right)^{1/2}$$

$$\approx 10^{-2} \left( \frac{kT}{\theta^2} \right)^{1/2} \left( \frac{d}{d^2} \right)^{1/2}$$

Equation (25) is identical to the result announced previously [1] up to the numerical prefactor which was not given. Note also that the correct value $\theta' = \theta/\xi$ instead of $\theta$ is used.

We now propose to go beyond equation (15) by keeping in a first step the expression (24) for $\langle u^2 \rangle/d^2$ and describing in a second step the cross-over to larger thicknesses (as done previously by comparing $d$ to $d_1$ and $d_2$) by introducing another mechanism which better takes into account the effect of shorter wavelength fluctuations. The idea (reported previously [1]) is to compare two characteristic time scales, namely, the relaxation time $\tau_r$ of concentration fluctuations and the typical time $\tau_s$ involved in shear constraints induced by large fluctuations interacting strongly with the substrate.

Only when the relaxation time $\tau_r$ is longer than the typical time $\tau_s$ will the shear appreciably disturb the concentration distribution and lead to a homogeneous behaviour.

It was thus predicted that this is the case for

$$\frac{\tau_s}{\tau_r} > 1$$

The relaxation time $\tau_r$ of concentration fluctuations is of the order of $\tau_r \sim \xi^2/\nu D$ where $\xi$ is the thermal correlation length and $D$ the diffusion constant. $\tau_s$ is the inverse of the mean shear $S = \eta q^2$ where $\eta$ is the kinetic viscosity and $q \sim \pi/d$ is of the order of magnitude of the mean wave vector of the velocity gradient. Inequality [26] then reads:

$$\frac{\xi^2}{\nu D} \frac{q^2}{\eta \pi^2} > 1$$

leading to

$$d < d_0 \sim 3 \xi$$

by taking the bulk transport properties of $^3\text{He}$ in inequality (27).

This effect limits the importance of fluctuations for thick films and thus predicts a stratified behaviour even in the presence of a large $\langle u^2 \rangle/d^2$ for $d > d_0$.

Our experiments indicate rather that $d_0 \sim 4-5 \xi$ where $\xi$ the correlation length is of the order of the atomic scale. Note that this alternative description amounts to replacing the equation (15) plotted in figure 3 by the simplified form (24) cut off at $d = d_0$. This corresponds to introducing two parameters $S$ and $d_0$ embodying the incertainty in the determination...
of the precise form of the bell-like curve shown on figure 3 and replace it by the curve presented figure 8. This additional assumption can now be tested.

Using the simplified expression (24) for \( \langle u^2 \rangle /d^2 \), we can predict that the necessary condition for the disappearance of a stratification is no longer fulfilled if \( \langle u^2 \rangle /d^2 < S \).

As a consequence, at a fixed thickness \( d \), the homogeneous-stratified transition should occur by lowering the temperature \( T \) below \( T^* \) given by

\[
10^{-2} \left( \frac{\kappa^2}{\Theta' \beta} \frac{T^*}{d^2} \frac{\alpha}{\alpha'} \right)^{1/2} = S. \tag{29}
\]

This relation implies that the product \( T^* d \) is proportional to the surface tension \( \alpha \).

\[
T^* d = A \alpha. \tag{30}
\]

We have plotted in figure 9, \( T^* d \) determined from the set of curves shown in figure 7 as a function of \( d_3 \). Note that \( T^* d \) decreases linearly with \( d_3 \) up to \( d_3 = 1 \) layer and then stays constant for higher \(^3\)He coverage. This was expected on the basis of equation (30) indicating that \( T^* d \) decreases from \( A \alpha_4 \) (extrapolated at \( d_3 = 0 \)) to the value \( A \alpha_3 \) reached for \( d_3 = 1 \).

Note also that the ratio \( \alpha_4 / \alpha_3 = 2.2 \) obtained from the curve in figure 9 is in good agreement with the ratio of the surface tension of \(^4\)He liquid-gas and \(^3\)He liquid-gas interfaces given in the literature for bulk system:

\[
\frac{\alpha_4}{\alpha_3} = 2.47. \tag{31}
\]

Furthermore, for higher \(^3\)He coverage (\( d_3 > 1 \)), \( T^* d \) stays at the constant value \( A \alpha_3 \), a result consistent with our model. To our knowledge there is no independent determination of the surface tension for films whose \(^3\)He content range from 0 to 1 atomic layer, which would have permitted a comparison with our measurement. Note however that the quasi-linear variation corresponds to an ideal mixture which is different from the behaviour of \(^3\)He on bulk \(^4\)He [17].

Let us finally mention another set of experiments already published, which are also consistent with our model.

Remembering that the normalized relative square displacement \( \langle u^2 \rangle /d^2 \) is proportional to the temperature \( T \) (15), it is expected to observe only stratified mixture films at low temperatures. In this respect we can analyse previous determinations of superfluid onset temperatures determinations performed on mixture films for four different constant coverages (Fig. 10). From the Kosterlitz, Thouless and Nelson theory, at the superfluid transition \( T_{\alpha} \), the ratio \( \sigma_{\alpha}/T_0 \) is constant, \( \sigma_{\alpha} \) being the areal superfluid density. At low temperature in a layered mixture film, the superfluid phase is pure \(^4\)He, and the \( \sigma_{\alpha} \) value is only fixed by the number of \(^4\)He atoms \( n_4 \) adsorbed by unit area [17]. Thus in the stratified regime, mixture films which correspond to the same \( n_4 \) value should be characterized by the same onset superfluid temperature. We have represented figure 10 different curves (dashed lines) at constant \( n_4 \). At low temperatur
Experimental determination of the superfluid onset temperature in film mixtures for four different constant total coverages which correspond to respective film thicknesses (in atomic layers) of 6 (lozenges), 5.1 (full circles), 4.2 (open triangles) and 3.4 (open circles). The dashed lines are the curves corresponding to constant amount of $^4$He (labelled in equivalent thickness $d_4$). At low temperature $T \approx 0.1$ K the curve $n_4 = 0.21$ at $\AA^{-2}$ ($d_4 = 2$) defines the same onset superfluid temperature for each set of experiments as expected in the stratified regime. On the other hand as the temperature is raised thermal fluctuations become important destroying the stratification in mixture films whose thickness is smaller than $d_0$, and the curves at constant $n_4$ define very different onset superfluid temperatures.

4. Summary and conclusion.

We have presented a model for describing stratified $^3$He-$^4$He mixture films as a multilayer system. The contributions to the free energy have been discussed. It was shown that the surface variation of the layers and the interactions between the layers which are similar to a compression energy are the two major ingredients of the free energy. The mean square displacement of a layer $\langle u^2 \rangle$ has been evaluated. We then assumed that the relative magnitude of $\langle u^2 \rangle^{1/2}$ with respect to the film thickness $d$ separates two domains. For small fluctuations $\langle u^2 \rangle/d^2 < S$ we get an unperturbed stratified system, while in the opposite case the homogeneous behaviour is observed. The model then predicts, at a given temperature, that for thin films $d < d_1$ the film will be stratified. For a range of thicknesses $d_1 < d < d_2$ the magnitude of fluctuations is sufficiently large so that one should observe a homogeneous behaviour. Finally for $d > d_2$ we find a stratified structure. At very low temperature all films will be stratified. This behaviour seems only qualitatively in agreement with experiments. A quantitative description of the experimental results requires a modified version of the model. We still suppose that the model is valid for small thicknesses but we introduce an additional cut off thickness $d_0$ above which the fluctuation magnitude is negligible. We then have a 2 parameter model.

Third sound measurements at $T = 0.4$ K for various thicknesses give the regime change and a value of $d_0$. The transition temperature for a set of films with constant $^4$He coverage $d_4 = 2.9$ atomic layers shows unambiguously a decrease of the transition temperature when the total coverage increase. Evaluation of $S$, the limit value of $\langle u^2 \rangle/d^2$ from one regime to the other, then gives reasonable values for the surface tension. Finally the analysis of the superfluid onset temperature for various mixtures films within the Kosterlitz-Thouless model are also well described with this fluctuation picture, stratification at low temperature and homogeneous behaviour at higher temperature. Note, however, that the physical mixing mechanism leading to the homogeneous behaviour (fluctuation at the atomic level or convection at the thickness scale...) is not elucidated.

In conclusion, the introduction of fluctuations in stratified $^3$He-$^4$He mixture films describes correctly the structure of these films as deduced from third sound experiments. The model remains however limited and crude as it relies on two ad hoc parameters : $S$ (crossover) and $d_0$ (thickness cut-off). Is it possible to obtain them from a more microscopic approach ? We are presently developing such a model which views the stratified-homogeneous transition as a « drying transition ». The present approach in terms of multilayers essentially considers the importance of the mixing entropy which is taken into account in the « wetting-drying » formalism by the gradient term in the Landau-Ginzburg expansion for the chemical potential. The two points of view are equivalent, the « drying » approach allowing however more precise predictions of the behaviour of the film as a function of $^3$He and $^4$He thicknesses. These new results will be presented in a forthcoming publication.
References

[14] We experimentally found the FHH equation to be valid in a wider thickness range than observed by Chen et al. (ref. [12]). This could explain the larger value of $\theta$ which arises from our measurements.
[18] McQueeny et al. (Ref. [16]) have shown that the normal phase proximity affects the superfluid density only in a very narrow region (about 0.5 atomic layer) near the interface.