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Stratification Transition in ^{3}He-^{4}He Mixture Films

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Third-sound measurements on ^{3}He-^{4}He mixture films at 0.4 K show a stratification which disappears when the ^{4}He thickness, i.e., roughly the interface distance to the wall, is less than 4.5 atomic layers. We propose to take into account for the stratification transition the influence of the steric interaction between the film interface fluctuations, the so-called ripplons, and the substrate. This effect, considered for the first time, allows definition of a crossover length d^* whose magnitude agrees with experimental determination.

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The success of the Kosterlitz-Thouless-Nelson[1] theory of vortex pair unbinding to describe the superfluid transition in thin ^{4}He films has provided a strong motivation for experimental studies of ^{3}He-^{4}He mixtures in reduced dimensions.[2–5] These experiments not only have demonstrated the validity of the Kosterlitz-Thouless theory to predict the superfluid transition in such mixtures but also have raised new, interesting problems. Among them are the variety of possible phase transitions which can occur in a system viewed as a two-dimensional (2D) mixture[6] or 2D Fermi fluid.[7] For one of these transitions, the phase separation, there is obviously different behavior depending on the thickness of the film, i.e., 3D or 2D regime. In 3D we expect a stratification in layers parallel to the wall, while in 2D there should be cluster formation of different concentrations. The transition from one regime to the other one is not yet fully described.

Specific-heat measurements[7] show evidence of cluster formation characteristic of 2D phase separation only for ^{4}He thickness lower than 4.2 atomic layers if the atomic layer is expressed as a physical distance of 3.6 Å, as in this Letter. Third-sound experiments[5] show, already at $T = 0.4$ K, a stratification in thin films of ^{3}He-^{4}He mixtures for ^{4}He coverages $\simeq 5.7$ atomic layers. The experimental results of third-sound velocity were effectively described by the assumption of a complete phase separation, ^{4}He phase near the walls and ^{3}He phase at the free surface. However, third-sound measurements for mixture films with lower ^{4}He coverages did not show such a stratification at the same temperature.[4] These experimental results raise a very interesting question about the possibility of stratification, i.e., a 3D phase separation with a boundary between two phases in thin films. Obviously this question is related to the thickness of the film. Of course we expect to go from 3D to 2D behavior by decreasing the thickness. Moreover, we must take into account the effect of the wall boundary which has been studied recently[8] and can, because of the interface fluctuations, prevent the stratification below a critical thickness.

The goal of this work is to study at $T = 0.4$ K the influence of ^{4}He coverage on the stratification. We use a third-sound resonator filled with Nuclepore filters in a ^{3}He-^{4}He dilution refrigerator. Between two copper cylinders (1.2-cm i.d., 3.7-cm o.d. and 2.4-cm height) we establish our resonance cavity, filled with 1800 Nuclepore filters adjusted to the cavity dimensions; a Plexiglas plate covers the top surface. The typical pore size is 0.2 μm and the total surface adsorption area is 57.7 m^2. The Nuclepore filter is a very interesting material which has been studied by Chen *et al.*[9] Not only does it have a very large surface adsorption area but it has been shown[9] also that capillary condensation occurs for coverage larger than 55 Å. It is therefore possible to study a very large range of thicknesses easily. The surface adsorption area and the thickness are estimated by following the standard technique described previously.[10] From the ^{4}He adsorption isotherm, we get a van der Waals constant of the Nuclepore material of $\theta = 50$ K (layer)^3.[10]

Two strips of Ag and Al, which are, respectively, the third-sound emitter and the receiver thermometer, are evaporated on a Nuclepore filter. Resonance in the film is generated by continuously driving 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 lockin 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 ^{4}He agrees with the usual third-sound velocity dependence. We also verify that a variation of heat power by a factor of 10 does not change our results.

We first study the third-sound velocity as a function of the ^{3}He coverage at $T=0.4$ K for two different ^{4}He coverages ($d_4=2.9$ and $d_4=6.2$ atomic layers). The results are presented in Fig. 1 as $C_3^2(d_3,d_4)/C_{30}^2(d_4)$, where C_3 is the measured third-sound velocity of the mixture film while C_{30} is the measured third-sound velocity of a ^{4}He film with the same ^{4}He thickness d_4. The measured values of C_{30} 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 ^{4}He 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.[4] 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 ^{4}He coverage because of capillary condensation which occurs in the crushed glass. On the same figure are also presented two theoretical curves for C_3^2/C_{30}^2, with the assumption of either stratification or homogeneous behavior.

In the case of stratification the calculation of Ellis *et al.*[5] gives, in the limit of complete separation, the relation

$$\frac{C_3^2}{C_{30}^2}=1-\frac{n_3}{n_4}+\frac{n_3/n_4}{(1+d_3/d_4)^4}, \tag{1}$$

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 behavior we have[4]

$$\frac{C_3^2}{C_{30}^2}=\frac{\sigma_s(X,T)}{\sigma_s(0,T)}\,\frac{\rho(0)m(0)}{\rho(X)m(X)}\left[\frac{d_4}{d_3+d_4}\right]^4, \tag{2}$$

where the mass m and density ρ depend on ^{3}He molar concentration X. The superfluid mass per unit area σ_s is evaluated as in Ref. 4.

The theoretical curves presented in Fig. 1 are obtained from Eqs. (1) and (2). 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 behavior (Fig. 1). For the largest ^{4}He coverage (6.2 layers) the experimental points suggest instead a stratification in the mixture film (Fig. 1). This result confirms the starting hypothesis that there is a strong influence of coverage which prevents 3D phase separation when the coverage is too low.

The two sets of experiments were done with quite different thicknesses in order to characterize clearly the two kinds of behavior, homogeneous or stratified. The next step is of course to study more accurately this 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 Fig. 2 as C_3^2/C_{30}^2, with the theoretical curves still obtained from Eqs. (1) and (2). The experimental points leave the

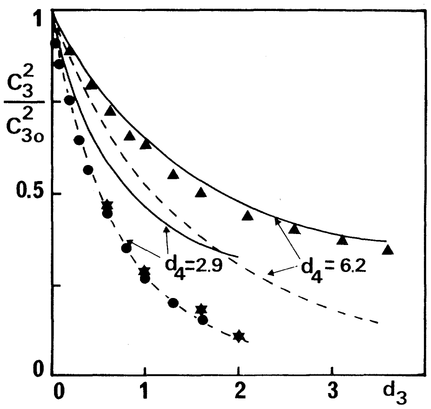

FIG. 1. Square of the relative third-sound velocity at 0.4 K as a function of ^{3}He coverage. The full lines and the dashed lines represent respectively Eq. (1) (complete phase separation) and Eq. (2) (perfect mixing) for each ^{4}He coverage. Experimental values were obtained from a time-of-flight technique on a glass substrate (circles) and with use of a resonator filled with Nuclepore filters (triangles and stars).

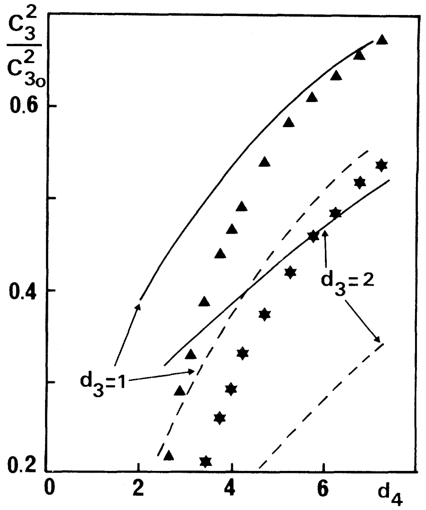

FIG. 2. Square of the relative third-sound velocity at 0.4 K as a function of ^{4}He coverage. The full lines and the dashed lines represent respectively Eqs. (1) and (2) for each ^{3}He coverage. Experimental values are obtained by use of a resonator filled with Nuclepore filters: $d_3=1$ (triangles) and $d_3=2$ (stars).

theoretical curve of stratification for $d_4 \lesssim 4.5$ layers and approach the homogeneous behavior. By comparing our results for the two ^{3}He coverages we find that it is the ^{4}He coverage and not the total coverage which is involved in the change of regime.

In order to rationalize our experimental results, we now propose a qualitative argument which introduces a new physical feature not considered previously. The discussion starts from the recognition of the importance of the interaction between the ^{3}He and ^{4}He as well as the ^{3}He-gas interface fluctuations, the so-called ripplons, and the substrate wall boundary.

Let us consider the mean square deviation $\langle z^2 \rangle$ of an isolated interface from its mean position, due to thermal and quantum excitations. A classical result[11] predicts $\langle z^2 \rangle$ as being proportional to $(kT/\sigma)\ln(L/l)$, where k is the Boltzmann constant, T is the temperature, σ is the surface tension of the two interfaces, L is the typical size of the interface, and l is a microscopic scale of the order of an atomic radius. Typically, for He around 0.4 K, we find $\langle z^2 \rangle^{1/2} \sim 6$ Å for $L \sim 0.2$ μm. As a result, for large film thickness or low temperatures such that $d >> \langle z^2 \rangle^{1/2}$, the interface undergoes free fluctuations whereas for thin films or higher temperatures ($d \lesssim \langle z^2 \rangle^{1/2}$), its wanderings become highly constrained. Using a simple classical picture, one of the authors has developed a calculation for this effect, which employs an interface displacement model[8] in which one writes an effective Hamiltonian for the location $z(\vec{r})$ of the interface as a function of the coordinate $\vec{r}(x,y)$ parallel to the wall. The effective Hamiltonian is the sum of the usual surface-tension contribution plus a compression term describing the repulsive steric interaction between the wandering interface and the rigid boundary. Within this model,[8] the influence of the van der Waals interaction can be taken into account by defining a "mean-field" effective compression modulus $(\theta/d^3)l/d$, where θ is the van der Waals constant, which yields

$$\langle z^2 \rangle \sim \left[\frac{(kT)^2}{\sigma l^2 \theta}\right]^{1/2} \left[\frac{d}{l}\right]^{1/2} d^2 \tag{3}$$

up to a model-dependent numerical factor of the order of 10^{-1}. As expected in this thin-film regime, the external field reduces the rms amplitude of the fluctuations down to $\langle z^2 \rangle^{1/2} \sim 0.2d$, the d-dependence stemming from the $1/d^3$ van der Waals law. It has been shown[12] for several models describing an interface constrained between two rigid walls in the excluded volume regime, that is for a high density of interface-wall "collisions," that $\langle z^2 \rangle^{1/2} \sim (0.3\text{–}0.6)d$. The reason is that even in the presence of many "contacts," a large portion of the interface still remains apart from the substrate. Consequently, it is plausible that in our helium films, the order of magnitude for $\langle z^2 \rangle^{1/2}$ derived from Eq. (3) still implies the existence of numerous collisions. Their density, which decreases exponentially with d in the range $d >> \langle z^2 \rangle^{1/2}$, is weakly d dependent for $d \lesssim \langle z^2 \rangle^{1/2}$.

We are now in a position to discuss the relevance of the ripplon-wall interaction for the homogeneous-stratification transition of the ^{3}He-^{4}He thin-film mixture, with increasing thickness d of the film.

These interface fluctuations induce velocity fields which for free fluctuating surfaces vary typically over a distance of the order of the excitation wavelength. Now, when contacts between the interface and the substrate exist, they induce stringent boundary conditions for the velocity field, which, as a consequence, must vary appreciably over a distance of the order of the film thickness d.

These fluctuation-induced velocity gradients or shear S perturb the concentration profiles of ^{3}He and ^{4}He in the film on a typical time scale $\tau_s = 1/S$, with $S = (\eta/\rho)q^2$ where η/ρ is the kinetic viscosity and $q \sim \pi/d$ is of the order of magnitude of the mean wave vector of the velocity gradient. As discussed initially by Onuki and Kawasaki[13] in another context, this time scale must be compared with the relaxation time $\tau_c \sim \xi^2/D$ of the concentration fluctuations, where ξ is the thermal correlation length and D is the diffusion constant.

We can intuitively predict the main characteristics of the effect of the shear on the concentration profiles as follows. Only when the relaxation time τ_c is longer than the typical time τ_s associated with shear will the shear appreciably disturb the concentration distributions. We thus predict an effect which will disturb the stratified layers for $S\tau_c > 1$, i.e.,

$$\pi^2(\eta/\rho D)(\xi/d)^2 > 1. \tag{4}$$

In the range of temperature $T \sim 0.2\text{–}0.6$ K, all ^{4}He is essentially superfluid. Hence, its relaxation response is extremely rapid and condition (4) is certainly not fulfilled for ^{4}He. However, for sufficiently high ^{3}He coverage ($d_3 \sim 1\text{–}2$), using for ^{3}He the bulk transport properties,[14] we get

$$\pi^2(\eta/\rho D)(\xi/d)^2 \sim 9(\xi/d)^2. \tag{5}$$

This result implies the existence of a crossover from a regime ($d > d^* \sim 3\xi$) dominated by the natural diffusion of ^{3}He, which under the external van der Waals field tends to separate from ^{4}He, to a regime essentially dominated by the fluctuation-induced shear ($d \lesssim d^* \sim 3\xi \lesssim \langle z^2 \rangle^{1/2}$). For systems far from the tricritical point, ξ is of the order of the molecular scale, which yields $d^* \sim 3$ atomic layers in good agreement with the experimental value ($d^* \sim 4$–5) considering the qualitative nature of the argument.

This reasoning may be further tested by examination of the temperature behavior of the stratification transition. We have checked that for the two thicknesses $d_4 = 2.9$ and $d_4 = 6.2$, we still get at $T = 0.5$ K the two different behaviors (homogeneous or stratified). However, a change of behavior of the third-sound velocity has been observed[4] at low temperatures, $T \sim 0.2$ K, for $d_4 = 2.9$. This effect observed for thin films can be explained within the framework of the present model: either criterion (4) is no longer fulfilled because of the variation of η and D with temperature and concentration, or $\langle z^2 \rangle^{1/2}$ eventually drops below the film thickness d with the result that the interface-substrate contacts disappear and the velocity gradient vanishes. A more quantitative test of this idea applied to such low-temperature regions is needed and a systematic study of this behavior is now under way.

We now briefly discuss the possible relevance of the ripplon-substrate interaction for third-sound propagation in pure ^{4}He films which have a liquid-gas interface. As already emphasized, the interface-substrate collisions can be phenomenologically described by an effective repulsive steric interaction[8] which mainly affects and hinders the amplitude of the long-wavelength modes. This makes plausible the existence of a rotonlike branch in the ripplon spectrum appearing for sufficiently thin films, which could be relevant in the explanation of the dependence of the superfluidity density on the film thickness.[15] The analysis of this problem is now under active study and will be presented elsewhere.[16]

Lastly, the ripplon-wall interaction may be an important mechanism giving rise to a large attenuation for thin films. A similar picture has been developed by Chester and Maynard[17] who have stressed the importance of the nonlinear coupling between the ripplons and the third-sound disturbance.

In conclusion, our new experimental results clearly show the existence of a crossover length below which stratification in the mixture films disappears. This effect results from the interaction between the interface fluctuations and the substrate.

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