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Approach to complete wetting in $^4$He-$^3$He binary liquid mixtures

D. Sornette (†) and J. P. Laheurte

Laboratoire de Physique de la Matière Condensée, associé au CNRS (UA 190), Université de Nice, Parc Valrose, 06034 Nice Cedex, France

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1. Introduction.

Three phases (A), (B), (C) in coexistence can exhibit very interesting phenomena such as wetting, prewetting and surface transitions, etc [1]. On the (C) rich side of the coexistence curve of phases (B) and (C), wetting is characterized by the appearance of a macroscopic thick film of one phase (B) intruding between the substances (A) and (C). (B) is then said to wet (A). A wealth of experimental and theoretical studies have given considerable insight leading to the classification of the different possible mechanisms (existence of a wetting transition, the nature of this transition, prewetting, dynamics of wetting, role of long-ranged forces, etc [2].

Here, we address this last point (role of long-ranged forces) and present experimental results carried on in our group a few years ago [3] but reinterpreted within the wetting approach. We show how the study of the « nucleation » of superfluidity and phase separation at walls in liquid $^3$He-$^4$He mixtures allows one to obtain the exponent of the adsorption in the approach to complete wetting in a system with long-ranged (Van der Waals) forces. We verify the powerlaw: adsorbed thickness of $^4$He = $(\delta T)^{-1.5}$ where $\delta T$ is the distance to bulk coexistence. This powerlaw has been verified in several systems using different techniques [4-6] but liquid helium affords the opportunity of studying very thin, extremely pure films. We thus verify that, contrary to a recent warning [7] this law remains valid for the He system, down to wetting layers thicknesses as small as five atomic layers.

The paper is organized as follows. In section 2, we recall several theoretical models accounting for the adsorption and reanalyse two of them for comparison with the experimental data. In section 3, the experiments are presented and their interpretation is given quantitatively in terms of a thermodynamic model. Finally, we conclude in section 4 with some general remarks concerning the specific features of the adsorption in helium systems.

2. Theoretical background.

Three main ingredients are necessary for describing a wetting transition:

a) the generalized free energy $w(\phi)$ of the bulk system as a function of its order parameter (concentration) $\phi$. 

(†) Also at Collège de France : Laboratoire de Physique de la Matière Condensée (CNRS UA 792), 11, Place Marcelin Berthelot, 75231 Paris Cedex 05, France.
b) the cost in free energy associated with concentration inhomogeneities as they occur in wetting phenomena (at the (B)/(C) interface).

c) the effect of the proximity of the wall.

In the He\textsuperscript{3}-He\textsuperscript{4} system, the interaction potentials between atoms are difficult to estimate because of a hierarchy of effects:

(i) the strong direct short-range forces between atoms.

(ii) the influence of zero-point motions which are different for the lighter \textsuperscript{3}He and for the heavier \textsuperscript{4}He.

(iii) the effect of the Pauli exclusion principle which induces a short-range correlation between \textsuperscript{3}He atoms carrying parallel spins.

(iv) the indirect \textsuperscript{4}He mediated \textsuperscript{3}He-\textsuperscript{3}He interaction.

A detailed analysis of the interactions can be made [8] in the homogeneous case. The extension to inhomogeneous fluids awaits further work. However, the short-range interactions seem to be the dominating factors for the local structure of the \textsuperscript{3}He-\textsuperscript{4}He mixtures whereas the long-range attractive forces act as a perturbation [8]. Furthermore, long-range forces can change the correlation significantly only in the unbound directions parallel to the substrate and not in the direction perpendicular to substrate due to the smallness of the thicknesses (5.20 at.1.). Also, the He-He Van der Waals interaction potential is roughly \textasciitilde\textasciitilde 2 K (layers) [3] to be compared to the He-substrate Van der Waals potential typically \textasciitilde\textasciitilde 30 K (layers) [3]. Therefore, in the mean field treatment where fluctuations and capillary modes are neglected, it appears plausible to consider relatively « universal » models in which the long-range Van der Waals fluid-fluid interaction acts only as a perturbation.

Various models [3, 9-19] can predict the divergence law of a wetting layer as coexistence is approached. We will briefly present the simplest one which gives the leading behaviour.

It was initially introduced by De Gennes [9] and put on a firm basis by introducing the interface displacement model [10]. It assumes that the most important contributions to the excess free energy per unit area associated with the (B) layer, being of finite thickness \(e\) rather than macroscopic, are:

i) a Van der Waals term \(\frac{\theta}{e^2}\) where \(\theta\) is positive and depends on the polarizabilities of the bulk phases [20] (term c).

ii) A chemical potential contribution \(\delta \mu e\), \(\delta \mu\) is the difference of chemical potential between phase (B) and phase (C) (term a).

\[
\delta \mu = \frac{\partial \mu}{\partial T} \cdot \delta T
\]

if the system is away from the coexistence curve by \(\delta T\). \(\delta \mu = \Delta \rho \cdot g L\) for a system of two phases in thermodynamic equilibrium with different densities \((\Delta \rho = \rho_B - \rho_c > 0)\) and immersed in a gravitational field \(g\). \(L\) is the height of the column of phase (C) and (A) is the vapour phase in this case. Term \(b\) is the (B)/(C) surface tension energy which is taken constant.

Minimizing \(\frac{\theta}{e^2} + \delta \mu e\) with respect to \(e\) yields the equilibrium thickness:

\[
e = \left(\frac{2\theta}{\delta \mu}\right)^{1/3}
\]

This approach allows us to treat the case of short-range forces. In this case, the Van der Waals contribution is replaced by a term \(V e^{-\delta \mu}\).

Minimisation of \(V e^{-\delta \mu} + e \delta \mu\) yields a logarithmic divergence as \(\delta \mu \to 0\):

\[
e \sim \xi \log \frac{V}{\delta \mu}
\]

This expression has recently been argued to be valid and verified by a computer simulation [12] even in 3d when fluctuations were included.

Other theories like those of Cahn and Sullivan [13-15] are described in appendix (A) and used to derive the leading correction to (1) for comparison with experimental results. Also a thermodynamic model specific to He mixtures is analysed to get the coefficient in front of the power law in appendix (B).

Other theoretical approaches using a solid on solid model [16] or a lattice gas model [18] also agree with the asymptotic law (1). We refer to references [16-18] for further details.

3. Experimental results and discussion.

3.1. Experimental Results. — As demixing occurs near a wall, \textsuperscript{3}He atoms are replaced by \textsuperscript{4}He atoms, resulting locally in a jump in concentration \(\Delta X\), which induces a variation of the dielectric constant

\[
\Delta \varepsilon = (\varepsilon_4 - \varepsilon_3) \Delta X
\]

where \(\varepsilon_4 = 1.056\) and \(\varepsilon_3 = 1.042\) are respectively the \textsuperscript{4}He and \textsuperscript{3}He dielectric constants.

The challenge was to detect in a bulk \textsuperscript{3}He-\textsuperscript{4}He mixture such small dielectric constant variations occurring over a few atomic layers near the wall. It was possible to measure these variations by capacitive measurements. The technique has already been described in a preceding paper [3]. We just recall the salient features for clarity and completeness.

Using vacuum evaporation and photoetching we obtained a set of 3 000 capacitors on a glass substrate (\textsuperscript{2}). The capacitor plates are 0.08 mm thick evaporated chromium electrodes. The mean distance between two electrodes is 2 mm and the developed capacitor length is about 60 m. In vacuum at 2 K the value of the system capacitance is about 2 000 pF. This value includes two contributions, the capacitive contribution of the upper field lines (only 15\% of the whole capacitance), and the capacitive contribution of field lines propagating in the glass substrate.

\(\textsuperscript{2}\) Chromium-evaporated substrates, Balzers, type LRC 300.
Obviously only the capacitive contribution of the upper field lines are affected by the presence of fluids. The substrate capacitance contribution is of course fluid independent and will represent a background.

The capacitance variations were measured with the G.R. Model 1615 capacitance bridge using a PAR 124 as voltage null detector. The bridge was used in a three-terminal mode with coaxial leads all the way between bridge and capacitance system. Connecting an external standard capacitance allows the bridge resolution to be increased in order to detect \(0.5 \times 10^{-3}\) pF.

The capacitive system was calibrated from isothermal \(^4\)He adsorption measurements. It was found that a dielectric constant variation \(\Delta \varepsilon\) occurring in a region of thickness \(e\) near the wall results in a capacitance change \(\Delta C\) defined by

\[
\Delta C = 0.2 \, e \, \Delta \varepsilon
\]

(\(\Delta C\) in pF ; \(e\) in atomic layers). The measurement gives information on the product \(e \, \Delta \varepsilon\) only. The knowledge of the phase separation diagram then gives at each temperature \(\Delta X\) from which \(\Delta \varepsilon\) is obtained (Eq. (3)). For instance at very low temperatures where \(\Delta X \approx 1\), resolution of this method makes it possible to detect the formation of 0.2 layer.

Figure 1 shows the capacitive variations as a function of temperature for two mixtures whose \(^3\)He concentrations are respectively 0.875 and 0.960. The mixture \(X = 0.960\) is stable in this range of temperatures and the capacitance variations arise from two contributions: first the substrate capacitive contribution, of course independent of the mixture, and second the contribution related to the temperature dependence of the dielectric constant \(\varepsilon_3\) and \(\varepsilon_4\). The latter contribution is negligible compared to the first one. So it appears that for stable mixtures the capacitance variations are concentration independent: in fact it was observed that the two experimental curves (Fig. 1) are identical above 0.595 K. Then the curve corresponding to \(X = 0.960\) can be considered as a continuous background from which are measured the capacitance variations \(\Delta C(T)\) induced by the growth of the separated phase. From the calibration of the capacitive system it is known that the increase \(\Delta \varepsilon\) of the separated phase thickness is related to \(C\) by [3]:

\[
\Delta \varepsilon = \frac{\Delta C}{0.2 \, (\varepsilon_4 - \varepsilon_3) \, (X_1 - X_2)}
\]

\(X_1\) and \(X_2\) being the two (bulk) equilibrium concentrations of the separated phase at the temperature studied.

Therefore from the \(\Delta C(T)\) measurements it is possible to describe the growth of the separated phase near the wall.

In fact these experiments were not able to detect the very first phase separation nucleation (predicted at 0.79 K) as the concentration jump and therefore the capacitance variations are too weak to be detected. Moreover when the temperature was decreased from 0.79 K the capacitance variation resulting from the slow growth of the separated phase thickness was smeared in the substrate capacitive contribution. It is only near the bulk phase separation temperature (below 0.60 K), when the separated phase thickness increases rapidly with temperature, that the capacitance variations \(\Delta C(T)\) are detectable. This capacitor method is very useful in the vicinity of the transition.

3.2. DISCUSSION. — The experimental results for three different mixtures \(X_d = 0.875\), \(X_d = 0.809\) and \(X_d = 0.74\) show the growth of the \(^4\)He rich phase near the walls through the increase of capacitance.

One of these experiments \((X_d = 0.875)\) has already been analysed [3] using the continuum thermodynamic model with the numerical calculations. The other two experiments are analysed here in the same way. Obviously the thermodynamic model of continuum gives a reasonable agreement (Figs. 2-3-4).

We notice, for one experiment \(X_d = 0.74\), that the experimental error bars are larger. This comes from
the fact that the concentration of the new phase near the walls is already \( = 0.45 \) so that the density variation is small at the separation. Also very close to the phase separation temperature the theoretical fit is not so good. This fit is very sensitive to the exact location of the transition temperature \( T_{\text{ps}} \). A small error in \( T_{\text{ps}} \) will of course induce large inaccuracy when \( \Delta T = T - T_{\text{ps}} \) is small. For large capacitance variations we also expect serious problems in the analysis. The linear dependence between capacitance and thickness will not remain valid. First because the relationship between thickness and capacitance is not linear and linearization is only an approximation. Also since it is quite possible for large thicknesses of the new phase to collect in the corners of the capacitor due to « capillary condensation ». For each curve the experimental variation of the thickness is fitted at one point of each calculated curve. This fit is necessary because for large \( \Delta T \) the thickness variation with temperature is too small to be detectable in the accuracy limit of these experiments.

It is then possible to check the asymptotic behaviour.

\[
e = \frac{C_1}{\Delta T^{1/2}} + C_2
\]

where \( \Delta T = T - T_{\text{ps}}(X_d) \) and \( C_2 \) is the leading correction (see Appendix A).

We analyse the experimental results with a least squares fit method (Figs. 2-3-4). We get for \( X_d = 0.875 \), \( C_1 = 16.85 \text{ (at.l. \times mK}^{1/3}) \), \( C_2 = -0.166 \text{ at.l.} \) and the standard deviation \( (\Delta e^2)^{1/2} = 0.245 \). This fit is obtained by getting rid of the two smallest values of \( \Delta T \), \( \Delta T = 1 \) and 2 mK. For \( X_d = 0.809 \) we find \( C_1 = 18.21 \text{ (at.l. \times mK}^{1/3}) \), \( C_2 = 0.019 \text{ at.l.} \) and \( \sqrt{\Delta e^2} = 0.234 \text{ at.l.} \) Finally for the last experiment the analysis is not so easy because the experimental error bars are so large as explained previously. So we decided to fix \( C_2 = 0 \) and try a best fit with all points except the largest value \( \Delta T = 12 \text{ mK} \) which is obviously out of any fit. We find \( C_1 = 18.85 \text{ (at.l. \times mK}^{1/3}) \) and \( (\Delta e^2)^{1/2} = 0.9 \). Other fits obtained by getting rid of the first points for instance do not improve seriously.
the fit \((\Delta e^2)^{1/2} \rightarrow 0.84\) and do not change a great deal \(C_1, C_1 \rightarrow 18.37\).

It is interesting to notice that \(C_1\) remains almost constant for the three experiments.

The leading correction \(C_2\) is surprisingly small so the fit with only one parameter \((C_1)\) is sufficient.

This shows that the correction \(\frac{1}{3} \frac{A_1}{z^3}\) to the leading terms \(\frac{1}{2} \frac{A_0}{z^2}\) of the attractive wall-fluid potential is negligible down to thicknesses \(e > 5\) at.l., (see Appendix A, Eq. (25)). More precisely, \(\frac{A_0}{2z^2} + \frac{A_1}{3z^3}\)

can be written as \(\frac{A_0}{2(z - C_2)^2}\) for \(z \gg C_2\). The correction term can thus be viewed as caused by a displacement of the Van der Waals plane \((z = 0)\). From the data presented here and that of reference [3], the \(^3\)He-\(^4\)He wetting is well described by a pure \(z^{-2}\) Van der Waals attraction. This means that the surface energy contribution by expression (5) is very short-range (a few atomic layers).

The value of \(C_1\) can be estimated in the frame of the thermodynamic model, as follows. We define \(\mu_4(X_Z, T)\) the chemical potential of a \(^4\)He atom at temperature \(T\) with a \(^3\)He concentration \(X_Z\) at distance \(z\) from the wall. We note that \(\mu_4\) is of course not the average chemical potential \(\mu\) used in equation (1). We assume that the interface between the \(^4\)He rich and \(^3\)He rich phases is located at \(z = e\).

Then, in the \(^3\)He rich phase, the local concentration is \(X_{Z = e} = X_{PS}(T, P_e)\) where \(P_e\) is the local pressure and \(X_{PS}\) the equilibrium \(^3\)He concentration at phase separation.

At a large distance from the wall, \(X_{Z \rightarrow \infty}\) is equal to \(X_0\) (the original mixture concentration). The equilibrium condition reads.

\[
\mu_4(0, T) = \mu_4(X_{PS}(T, P_e), T) - \frac{\theta}{e^3} \tag{7}
\]

where \(\theta\) has been defined in § 2. Then

\[
e = \left(\frac{\theta}{\partial \mu_4 / \Delta X}\right)^{1/3} \tag{8}
\]

This behaviour is also related to the temperature difference

\[
\Delta T = T - T_{PS}(X_0, P_e) \tag{11}
\]

\[
e \approx \left(\frac{\theta}{\partial X/\partial T}_{eq} / \Delta X\right)^{1/3} \tag{12}
\]

where \(\partial X / \partial T\) \(\approx\) is the equilibrium curve for phase separation at pressure \(P_e\).

In these mixtures the equilibrium curves are [22]

\[
1 - X = 0.85 T^{0.2} \exp \left(-\frac{B}{T}\right) \tag{13}
\]

where \(B\) goes from 0.56 K at small pressure to \(B = 0.48\) K for \(P = 15\) atmosphere. Also the chemi-
cal potential of the quasiparticle gas of $^4$He is:

$$\mu_4 = -E_4 + K T \ln \left( \frac{1 - X}{V} \frac{2 \pi h^2}{m_4^* K T} \right)^{3/2}$$

(14)

where $E_4$ is a constant corresponding to a binding energy, while $m_4^*$ is the $^4$He effective mass. Substituting in equation (12) we finally get

$$e = \frac{\theta}{\left( \frac{3}{2} + \frac{B}{T} \right) \Delta T}$$

(15)

and

$$C_1 = \left( \frac{3}{2} + \frac{B}{T} \right)^{1/3}$$

(16)

Putting $\theta = 27$ (K) (at.l.) $^3 B = 0.55$ (K) and $T = 0.5$ (K) we find $C_1 = 22$ (at.l. x mK$^{1/3}$). This value is in good agreement with that obtained in the fit $C_1 = 19$ (at.l. x mK$^{1/3}$). We notice that $C_1$ is effectively almost constant for all experiments as $B$ does not change much with pressure, and as the temperature dependence of $C_1$ (Eq. (16)) is also weak.

4. Conclusion.

We have considered a previous study (3) on the adsorption of $^4$He atoms on a substrate in a $^3$He-$^4$He mixture. We have demonstrated the remarkable accuracy of the fit of our experimental data by the powerlaw behaviour of the $^4$He adsorption thickness $e \sim (\Delta T)^{-1/3}$. The standard deviation is around 0.2 atomic layer, which is better than an angstrom.

This behaviour stems from the long-range Van der Waals potential existing between the substrate and the helium atoms. This potential changes the behaviour $e \sim - \ln \Delta T$ into the powerlaw $e \sim (\Delta T)^{-1/3}$. Note that the presence of the Van der Waals force also brings in a long range tail in the density profile [23] which has been analysed by other authors but which is not seen in our experiments.

The non-retarded Van der Waals potential $V \sim - \theta \pi z^3$ has been used in the analysis since the measured thicknesses range from around 5 to 20 atomic layers (20-80 Å). In other binary mixtures kept at room temperature, much larger thicknesses ($\sim$ 200-1 000 Å) have been measured for which the retarded Van der Waals potential $V_r \sim \theta \pi z^4$ must be used. This yields an adsorption thickness diverging as $e \sim (\Delta T)^{-1/4}$ at coexistence.

The striking feature of our data is the range of measured thicknesses (5 to 20 a.l.) for which very precise measurements can be made due to the great purity of the sample and the extreme sensitivity of the experimental method.

We have also recalled several theoretical models accounting for the adsorption. The interface displacement model is useful for its simplicity and universality. We have dwelt upon the Cahn model which allows a qualitative derivation of the leading behaviour of $e (\Delta T)$ [14] but also enabled us to estimate systematically the corrections to this leading behaviour. Lastly, the thermodynamic model developed previously in reference [3] has been reanalysed and shown to be equivalent to the other approaches. Furthermore, it allows a correct quantitative comparison with our data.

We now discuss some features specific to the helium system.

1. Unstabilities or hydrodynamic effects have not caused problems in the reported and other experiments carried out in our group. This seems to be due to the extreme smallness of the adsorbed films thicknesses.

Could quantum effects affect the adsorption? Indeed we expect to see more of the influence of the quantum nature of $^4$He atoms when temperature is reduced. However the $^4$He atoms are also less bound in a liquid rich in $^3$He than in one rich in $^4$He. The energy difference is $\approx 0.56$ K. So the $^4$He atoms leave the $^3$He rich phase towards the $^4$He phase when the temperature drops.

Then the average distance between two $^4$He atoms in the $^3$He concentrated phase will be large. It is directly linked to the average atomic volume $v$ and $^3$He concentration $X$ by $(v / (1 - X))^{1/3}$. The minimal value of $X$ is given by the phase separation curve (Eq. (13)). As $(1 - X_{PS}) \propto T^{3/2} e^{-B T}$, the average distance between $^4$He atoms in the $^3$He rich phase increases much faster when $T \rightarrow 0$ K than the thermal wavelength $(\lambda_T \propto T^{-1/2})$. Thus the $^4$He quasiparticle gas remains classical even when $T \rightarrow 0$ K.

2. The adsorption law $e \sim (\Delta T)^{-1/3}$ is a direct evidence that $^4$He completely wets the substrate (at coexistence). Is it also the case at lower temperatures?

We know that the wetting transition temperature is $T_w = 0$, if the interaction potential substrate-adatom is sufficiently large compared to the adatom-adatom potential [24]. The He-He interaction potential has been evaluated [25-26] $= 2.2$ to 2.7 K (layers$^3$) and should be compared to the Van der Waals potential strength of He with substrates [26] which is always much larger, typically $= 30$ K (layers$^3$), so we expect liquid helium to wet substrates down to $T = 0$ K.

3. In a related previous study [3, 27] one of us and co-workers have shown the existence of a superficial superfluid transition in the adsorbed $^4$He layer. It has been determined to be of the Kosterlitz-Thouless type i.e. corresponding to a defect (vortex) mediated transition instead of an order parameter
phase transition. The question arises whether the adsorption could be coupled to the superfluid appearance, as is the case for example for the phase separation in the vicinity of the bulk tricritical point. However, one can argue that the superficial superfluidity formation is a secondary effect of the $^4$He adsorption in a way similar to the appearance of a ferromagnetic ordering once the structure of a crystal is given. This also seems to be the point of view adopted by authors using the general theory of surface and special transitions [1, 28]. Note however that a recent Migdal-Kadanoff approach using a two-dimensional version of the model Blume et al. (BEG) [29] has predicted the existence of a critical point ending the line of Kosterlitz-Thouless film superfluidity formation and beginning a line of superfluid phase separation. In the vicinity of this critical point, one could expect departure from expression (1). Such an effect has been observed in binary mixtures [30] in the vicinity of the first order wetting transition and of the consolute point [5] where, for unclear reasons either the adsorption thickness $e$ varies slowly with $\delta \mu$ or with a different powerlaw exponent.

In our system, measurements near the tricritical point are very difficult because of the vanishing difference in concentration of the two separated phases. The existence of a critical point at low temperature [25] has not yet been experimentally observed and new experiments are certainly needed to check this prediction.

Acknowledgments.

We would like to thank Dr. J. P. Romagnan who is so deeply associated to this work. A discussion of the exponential corrections as discussed in Appendix A has also been carried on by R. Lipowsky, Z. Phys. B 55 (1984) 345. We are grateful to one of the referees for this point and other useful remarks.

Appendix A

Cahn-Sullivan theory [13, 15]. — Cahn’s theory only applies to systems with short-range fluid-fluid forces whereas Sullivan’s approach tries to consider the cases of long-range fluid-fluid forces.

They can both be cast into the same form by using the following expression for the inhomogeneous energy functional.

$$\gamma_d = \int_0^\infty dz \int_0^\infty dz' W(z-z') \phi(z) \phi(z') +$$

$$\int_0^\infty dz \left[ W(\phi) + \delta \mu \phi + \delta(z) W_s(z) \right]$$

In the mean field treatment, one has to minimize $\gamma_d$ with respect to the whole order-parameter profile $\phi(z)$. In Cahn’s theory, $W(z-z') = \delta^\ast(z-z')$ is proportional to the second derivative of the Dirac distribution. This yields the usual Landau-Ginzburg form $\int dz \frac{\xi}{2} \frac{(d\phi)^2}{dz}$ for the first term in the r.h.s of equation (17). Sullivan and other authors use a particular expression for $W(z-z')$ chosen for the sake of mathematical convenience [15]. Since the Sullivan approach can be treated analytically only for exponential interactions, the two models yield the same leading behaviour.

Depending on the model, the various parameters in equation (17) take different meanings. In Cahn’s model, $W(\phi) = f(\phi) - \phi \delta \mu - P$ where $f$ is the free energy density of the bulk phase, $\mu$ its chemical potential, and $P$ the pressure. Coexistence corresponds to two equal minima of $W(\phi)$ for two densities $\phi_1$ and $\phi_2$. The term $\delta \mu \phi$ weights the distance from coexistence. $W_s(\phi)$ is the additional wall contribution embodying the influence of short-range substrate-system interactions and localized at $z = 0$. If Van der Waals forces exist, one then adds a term

$$\int_0^\infty dz \frac{\theta}{z^3} \phi(z)$$

We give, below, the general solution of the minimization of equation (17) in the Cahn form, and its leading corrections.

Indeed, it seemed important to us to take these corrections into account for analysing our data which show thicknesses ranging from 5 to 25 atomic layers. However, as we show in the text, the leading behaviour is sufficient for fitting the experiments. We give however the structure of the corrections as they allow the order of magnitude of the correction to be estimated and also could be useful in other cases.

The order parameter profile is a solution of the Euler-Lagrange equation.

$$\xi \frac{d^2 \phi}{dz^2} = \frac{dW}{d\phi} + \delta \mu + \frac{\theta}{z^3}$$

$$\xi \frac{d\phi}{dz} \bigg|_{z=0} = \frac{dW}{d\phi} \phi(z=0)$$

Equation (18) has been analysed in detail by Privman [14] using a clever approximation scheme which amounts to introducing the effective thickness $e$ as an adjustable parameter determined by a self-consistent relation using equation (19). He finds the leading behaviour given by equation (1). He also claims that his procedure allows a systematic evaluation of the corrections to equation (1) but does not give them explicitly. For the sake of simplicity, let us assume that $\phi_1 = -M$ and $\phi_2 = +M$ and that $\delta \mu > 0$ favours $(-M)$. We then take $\theta < 0$ to describe the wetting of the substrate at $z = 0$ by phase $+M$. In the vicinity of $\phi = +M$, $W(\phi) =
Equation (18) then simplifies to:
\[
\frac{1}{2} \alpha (\phi - M)^2. \quad \text{Equation (18) then simplifies to:}
\]
\[
\xi \frac{d^2 \phi}{dz^2} = \alpha (\phi - M) + \frac{\theta}{z^2} + \delta \mu
\]

We can obtain the leading behaviour (1) from this equation with the following heuristic argument. Equation (20) is a non-autonomous second-order differential equation. However, for sufficiently small \(\theta\), using the particle analogy, equation (20) can be viewed as the equation of motion of a particle of « mass » \(\xi\), « position » \(\phi\) at « time » \(z\) in a time-varying potential. Using an adiabatic approximation [21], we obtain the approximate « time »-varying first integral:
\[
\frac{1}{2} \xi \left( \frac{d\phi}{dz} \right)^2 = \frac{1}{2} \alpha (\phi - M)^2 + \left( \delta \mu + \frac{\theta}{z^2} \right) \phi
\]

Since \(\phi \sim + M\), the kinetic energy \(\frac{1}{2} \xi \left( \frac{d\phi}{dz} \right)^2\) will be zero as long as \(\delta \mu + \frac{\theta}{z^2} < 0\). During this « time »
\(e \sim \left( \delta \mu \right)^{-1/3}\), the particle is stuck at position \(\phi \sim - M\). As soon as \(\delta \mu + \frac{\theta}{z^2} > 0\), the particle escapes to \(\phi = - M\) in a relatively short time \((- \log \delta \mu\).

We now discuss the correction to this law.

The general form of the solution of equation (19) is
\[
\phi (z) = M - \frac{1}{\alpha} \delta \mu + \frac{1}{2} e^{-z/\alpha} \int_{z_1}^{z} dt e^{\nu t} - \frac{1}{2} e^{-z/\alpha} \int_{z_2}^{z} dt e^{-\nu t}
\]
\[
\chi = \left( \frac{\xi}{\alpha} \right)^{1/2}
\]
and
\(z_1\) and \(z_2\) are two constants of integration determined by equation (19) and a condition of matching to the other branch \(\phi (z \to \infty) = - M\).

The leading behaviour of (22) at large \(z\) is
\[
\phi (z) = M = - \frac{1}{\alpha} \delta \mu + \frac{A_0}{z^3} + \frac{A_1}{z^4} + \ldots + e^{-z/\alpha} \left( \frac{B_0}{z^3} + \frac{B_1}{z^4} + \ldots \right)
\]

The wall is said to be wetted if at coexistence \((\delta \mu = 0)\), \(\phi (z \to \infty) = + M\). This implies as usual that the boundary condition (19) verifies \(\phi (z = 0) > M\). Away from coexistence \((\delta \mu \neq 0)\), we obtain the wetting layer thickness \(e\) up to a numerical factor by the condition \(e = z (\phi = M)\) which verifies
\[
\frac{1}{\alpha} \delta \mu = \frac{A_0}{e^3} + \frac{A_1}{e^4} + \ldots + e^{-z/\alpha} \left( \frac{B_0}{e^3} + \frac{B_1}{e^4} + \ldots \right)
\]
i.e.
\[
e \sim C_1 \delta \mu^{-1/3} + C_2 + C_3 \delta \mu^{1/3} + \ldots + e^{-\delta \mu^{-1/3}} \left( D_1 \delta \mu^{-4/3} + D_2 \delta \mu^{-1} + \ldots \right) + e^{-2 \delta \mu^{-1/3}} (\ldots) + \ldots
\]

Equation (25) again yields expression (1) as the leading term and shows the structure of the corrections. \(C_1, C_2, \ldots, D_1, D_2, \ldots\) are constants determined from the boundary conditions. In particular, \(C_2 = \frac{1}{3} A_1 / A_0\). Thus, an experimentally determined upperbound for \(C_2\) yields an upper bound for the correction to the leading form \(\frac{1}{2} A_0 \delta \mu^{-2} / z^2\) of the effective wall-fluid potential. One should be careful in noting that corrections of the form \(C_3 / e^4 + \ldots\) also stem from retardations to the Van der Waals interaction. \(C_2\) is typically a few atomic layers and we thus expect a departure from equation (1) when \(e \sim C_2\).

Other terms also appear from cubic and quartic corrections to the quadratic form taken for \(W(\phi)\) near \(\phi = + M\). Using a Ginzburg-like argument, their form in equation (24) is found to be \(\delta \mu \sim e^{-z/\alpha}\) with \(\chi' \sim \chi + 0 (M^2)\).

Appendix B

THERMODYNAMIC MODEL. — We now show that the thermodynamic model developed in references [3, 17] also yields the behaviour (1). It has been used with success in describing several features which have emerged in experiments on helium films.

The model relies on two assumptions:

1) The interfaces are ideally flat with zero thickness.
ii) Local thermodynamic variables may be used even on a scale comparable to the average interparticle spacing.

In this model, the Van der Waals interaction between the substrate and the He atoms is introduced in the chemical potential per atom. The thermodynamic equilibrium implies equality of the chemical potential of all atoms. This leads to the appearance of a $^3$He concentration $X(z)$ and a pressure $P(z)$ developing a spatial dependence. $z$ is as before the distance from the substrate.

From \( \nu = \frac{\partial \mu_i}{\partial P} \) giving the atomic volume of each species $\{i = 3 \text{ or } 4\}$ and the Gibbs-Duhem relation, one relates the work corresponding to a variation of pressure to the variation of Van der Waals energy:

\[
\nu \frac{\partial P}{\partial \nu} = -3 \frac{\partial \mu_i}{\partial P} \frac{dz}{z^4}
\]

whose solution is

\[
P(z) = P_\infty + 3 \int_{\nu, \infty}^{\nu(z)} \frac{dz}{z^4} - P_\infty + \frac{C}{z} + 0 \left( \frac{1}{z^3} \right)
\]

where $C$ is a constant.

An equation similar to (26) yields $X$ as a function of $z$:

\[
\frac{dX}{X(1 - X)} = -\frac{\Delta \nu}{\gamma k T} \frac{dP}{P_\infty}
\]

where $\nu$ is the average volume of an He atom in the mixture:

\[
\nu = \nu_3 + (1 - X) \nu_4
\]

while

\[
\Delta \nu = \nu_3 - \nu_4
\]

and

\[
\gamma = \frac{X}{X (1 - X)} \left( \frac{\partial \mu_3}{\partial X} \right)_{T, P}
\]

Equations (26), (27) and (28) yield $X(z)$ and $P(z)$. Eliminating $z$, this also gives $P(X)$. Note that a given $(X, P)$ corresponds to a unique distance $z$ from the walls at which the mixture is at concentration $X$ and pressure $P$.

The main assumption of the model is to compare the profiles $P_T(X)$ obtained from equations (26)-(28) to the coexistence diagrams and decide for instance that the transition from homogeneous to phase separation occurs locally when the bulk equilibrium conditions for the transition are fulfilled. This condition is:

\[
P_T(X) = P_{ps}(X, T) = P_\infty
\]

where $P_{ps}(X, T)$ is the pressure for the phase separation obtained from the literature.

In the same way for the superfluid transition we write:

\[
P_T(X) = P_{sa}(X, T)
\]

where $P_{sa}(X, T)$ is the pressure for superfluid transition in mixture.

Let us call $X_1, P_1$ the solution of equation (29). Then, the thickness $e$ of the adsorbed $^3$He phase is such that

\[
P(e) = P_1
\]

\[
X(e) = X_1
\]

As the coexistence is approached, $e \to \infty$, $P_1 \to P_\infty$, i.e. $P_1 - P_\infty \to 0$. If we approach coexistence at fixed mean concentrations, by varying the temperature, $\delta T = T - T_{ps} \to 0$, we expect

\[
P_1 - P_\infty \sim \delta T
\]

Then from equation (27) we obtain

\[
e \sim (\delta T)^{-\frac{1}{3}}
\]

References


