INCOMPLETE WETTING OF HELIUM FILMS *

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Incomplete wetting of adsorbed He films is treated by a classical liquid slab model near T = 0. Several contributions to the chemical potential at coexistence are examined: cohesion, adhesion, compression and solidification by the substrate field, and interfacial energies.

1. Introduction

The recent experimental study by Migone, Krim, Dash and Suzanne [1] which shows that He incompletely wets Au (111) and Ag (111) surfaces at temperatures from 1.4 K to the critical point extends earlier work on other surfaces and more limited temperature ranges [2]. The results cannot be understood in terms of current theories of wetting, which attribute this behavior to relatively weak substrate attraction [3] or to mismatch between crystal structures of film and coexisting bulk solid surfaces [4]. Neither mechanism can apply to He films, since their attraction to all solid substrates is relatively strong, and no mismatch can occur between the liquid film surface and the bulk liquid phase. This paper explore several contributions to the chemical potential at low temperature, indicating that the incomplete wetting is probably associated with the solidification of layers close to the substrate by the strong Van der Waals field, and the truncation energy due to finite thickness.

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2. Theory

2.1. Single-phase film

The film is modeled as a thin slab of thickness $L$ of bulk liquid on a smooth substrate with long-range Van der Waals attractive forces. For 3D compressibility $\kappa = \rho^{-1}(\partial \rho / \partial P)$, the 3D density within the film varies with local pressure $P$ as

$$\rho = \rho_0 \exp\left[ \kappa (P - P_0) \right], \quad (1)$$

where $\rho_0$ and $P_0$ are the values at the film-vapor interface. $P$ and $\rho$ vary due to the external potential $u(z)$ due to the substrate, according to the condition for hydrostatic equilibrium:

$$\nabla P + \rho \nabla u = 0. \quad (2)$$

The solution of (1) and (2) leads to

$$\rho(z) = \rho_0 \left( 1 + \kappa \rho_0 \left[ u(z) - u(L) \right] \right). \quad (3)$$

Wetting characteristics can be determined from the thickness dependence of the chemical potential $\mu_t$ of the film: the thickness $L_0$ at coexistence is given by the condition

$$\mu_t(L_0) = \mu_0, \quad (4)$$

where $\mu_0$ is the chemical potential of bulk liquid. $\mu_t$ is derivable from the general expression for the free energy per particle $f(\rho, T)$:

$$F = Nf(\rho, T), \quad \mu = \partial F/\partial N. \quad (5)$$

At $T=0$, $f = e(\rho)$, the energy per particle. For the compressible film in the substrate field, the energy per particle $e = v(\rho) + u(z)$, where $v(\rho)$ is the energy due to interactions within the film:

$$e = v_0 + u(z) + \Delta v. \quad (6)$$

where $v_0$ refers to uncompressed bulk and $\Delta v$ is the energy per particle due to compression. We find

$$\Delta v = \int P \, d\rho / \rho^2 = (\rho_0 \kappa) \left( 1 - \frac{1}{\rho_0} \ln \left( \frac{\rho_0}{\rho} \right) \right). \quad (7)$$

2.2. Two-phase films

We now allow for solidification of a thin layer of film close to the substrate due to the Van der Waals field. (The first one or several layers in experimental films are known to be solid, see e.g. ref. [2].) We apply an analysis similar to that in part A to a two-phase slab model, where solid extends over $0 \leq z \leq L'$. 


and liquid over \( L' \leq z \leq L \). Liquid and solid phases have distinct compressibilities and field-free densities \( \rho_{\text{el}} \) and \( \rho_{\text{m}} \). We locate the position of the liquid–solid interface by setting the pressure \( P(z) \) function in the liquid to the observed melting pressure \( P_m \) of bulk \(^4\)He. With \( u(z) = -\alpha/z^3 \),

\[
L' = \left( L - 3 + C_m/\alpha \right)^{1/3},
\]

where

\[
C_m = (\kappa_{\text{el}} \rho_{\text{el}})^{-1} \left[ 1 - \exp(-\kappa_{\text{el}} P_m) \right].
\]

In fig. 1 we graph \( L' \) versus \( L \) for various values of \( \alpha \). The calculation shows reasonable agreement with experimental values for graphite: \( L' = 2 \) at \( L_0 = 4 \) layers.

The chemical potential of the composite film is more complicated than eq. (6) since the total free energy contains contributions from the liquid and solid fractions and the liquid–solid interface. The liquid and solid "bulk" concentrations are

\[
F_{\text{sol}} = A \int_{L'}^L \Delta v_\ell (\rho_\ell, z) \rho_\ell(z) \, dz, \quad F_{\text{liq}} = A \int_{L'}^L \Delta v_\ell (\rho_\ell, z) \rho_\ell(z) \, dz.
\]

where \( \Delta v_\ell \) and \( \Delta v_s \) are the energy function (7) for each phase. The chemical potential of the film is obtained as a sum of liquid, solid, and interfacial terms:

\[
\mu(L) = \frac{\partial F}{\partial N} = \frac{\partial F_{\text{sol}}}{\partial N} + \frac{\partial F_{\text{liq}}}{\partial N} + \frac{\partial \Delta F}{\partial N} \left( \frac{\partial N}{\partial L} \right)^{-1},
\]

where \( \Delta F \) is the contribution due to the film–vapor and liquid film–solid film interfaces. The coexistence thickness is found, as in section 2.1, through the condition \( \mu(L) = \mu_0 \).

We solved for the bulk terms by numerical methods, using empirical values
Fig. 2. Chemical potential of the two-phase helium film (\( \mu_f \)) as a function of total film thickness (\( L \)) for substrate attractions corresponding to MgO, graphite, Au and Ag. Experiments indicate that the chemical potential of a helium film on graphite should intersect with the bulk chemical potential near 4 layers.

for the liquid and solid densities, compressibilities and melting pressure, and for a range of substrate potentials spanning typical experimental values.

The results are given in fig. 2. According to these calculations there must be an additional contribution to \( \mu_f \) at coexistence, amounting to 0.36 \( k_B \) for a four layer film on graphite.

We can now show that the interfacial terms, which are not included in the numerical results, give a contribution comparable to the missing \( \Delta \mu \). We estimate the surface energy as that due to truncation of the Van der Waals pair interactions due to finite film thickness. Compressibility and surface relaxation effects are neglected, and we assume a Lennard-Jones 12-6 potential

\[
\varepsilon(r) = -4\varepsilon_0 \left[ \left( \frac{\sigma}{r} \right)^6 - \left( \frac{\sigma}{r} \right)^{12} \right]
\]

for molecular separations \( r \geq \sigma \). We calculate the energy of an interface between a single-phase film of thickness \( L \) and a low density vapor:

\[
\Delta F = A\gamma \left[ 1 - \frac{2}{9} \left( \frac{\sigma}{L} \right)^2 \right], \quad \gamma = \frac{3}{4} \pi \varepsilon_0 \rho^2 \sigma^4.
\]  

We note here that the surface energy makes no contribution to \( \mu \) in the limit \( L = \infty \). For the two-phase film, there are three interfaces contributing to \( \Delta F \) at finite \( L \) and \( L' \):

\[
\Delta F = F_{\gamma\gamma} + F_{\infty} + F_{\gamma'}. \tag{12a}
\]

where

\[
F_{\gamma\gamma} = A\gamma_{\gamma\gamma} \left[ 1 - \frac{2}{9} \left( \frac{\sigma}{L} \right)^2 \right], \quad F_{\infty} = A\gamma_{\infty} \left[ 1 - \frac{2}{9} \left( \frac{\sigma}{L'} \right)^2 \right]. \tag{12b}
\]
The liquid–solid interfacial energy in our model is:

\[ F_{rr} = F_{r\gamma} + F_{s\gamma} - 2A\gamma_{r\gamma}s\gamma_{ss}\left[1 + \frac{2}{9}\left(\frac{\sigma}{L}\right)^2 - \frac{2}{9}\left(\frac{\sigma}{L'}\right)^2 - \frac{2}{9}\left(\frac{\sigma}{L-L'}\right)^2\right]. \]  \( (13) \)

Eq. (13), in the limit \( L, L' = \infty \), yields the combining law [6] \( \gamma_{r\gamma} = \gamma_{r\gamma} + \gamma_{s\gamma} - 2\gamma_{r\gamma}s\gamma_{ss} \). This approximation yields a much smaller value than the experimental result, \( \gamma_{r\gamma} = 0.16 \text{ erg/cm}^2 \) for \(^4\text{He} \) at low temperature [7]. We believe that the discrepancy is due to our neglect of compressional and relaxation effects at this interface, and indicates that the effective value of \( \sqrt[3]{\gamma_{r\gamma}s\gamma_{ss}} \) in eq. (14) is markedly reduced. With this empirical correction, eq. (12) yields in the region \( dL'/dL \approx 0 \):

\[ \Delta \mu \approx \frac{8}{9} \rho \frac{\sigma^2 \gamma_{r\gamma}}{(L-L')^3}. \]  \( (14) \)

Employing experimental values for \( \rho \approx 1/\sigma^3 \), and \( \gamma_{r\gamma} \), [5], we find \( \Delta \mu = 0.37 \text{ k_B} \) at \( L - L' = 2 \text{ layers} \), in reasonable agreement with the result for graphite.

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References

[5] W.E. Keller, \(^3\text{He} \) and \(^4\text{He} \) (Plenum, New York, 1969).