

CONDENSATION OF HELIUM IN WEDGES

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We investigate the adsorption of helium in alkali wedges at zero temperature within a fully unrestricted density-functional theory. We have found a sequence of shapes that includes one filling transition on the nonwettable Cs and one emptying transition for every alkali, as well as a threshold for metastable configurations where helium does not populate the wedge apex.

Keywords: Wedge geometry, wetting, filling and emptying transitions

1. Introduction

A variety of theoretical and experimental studies of the growth of adsorbed films have demonstrated that the geometry of a substrate exposed to a vapor phase plays a significant role in the wetting behavior of the fluid. While on a planar surface the growth is governed by the interactions between adatoms and between adsorbate and substrate, on real surfaces exhibiting steps, corners, stripes and other manifestations of disorder that may give rise to roughness, randomness and even fractality, the liquid-substrate interface adjusts to the local imperfections to keep the surface free energy at a global minimum.¹⁻⁵ Experiments on X-ray scattering at grazing incidence can resolve such interfacial structures.⁶ Current manufacturing techniques are in use in nanofluidics, where very small amounts of fluid are stored and may flow in narrow channels,⁷ and various experimental methods permit the creation of structured or imprinted surfaces within the micrometer scale.⁵ Moreover, using chemical patterning one can control fabrication at the nanoscale⁸ and for some applications involving structured semiconductor surfaces, highly regular, although nonhomogeneous surface structures can be produced (see, *i.e.*, Ref. 3). It is then

of interest to investigate adsorption of liquid films on structured substrates in the nanoscopic, mesoscopic and macroscopic domains.

Since the early 90's, it has been pointed out that wedge wetting may constitute a paradigm for nontrivial interfacial profiles, and it has been recently suggested that fluids adsorbed in a planar wedge can be regarded as a generic class of structured inhomogeneous fluids.⁹ In a series of papers, Parry and coworkers (see 10,11 and refs. cited therein) have shown that the wedge geometry introduces classes of interfacial phase transitions, giving rise to a family of interfacial critical phenomena controlled by the geometric parameters that define the structured surface. As a speculation,¹² it has been also suggested that wedge-like geometries might offer the possibility of observing effects of prewetting. From the experimental viewpoint, adsorption of Ar on patterned Si⁴ shows that the crossover between a planar and a geometrically dominated regime is similar to that found numerically by Rascón and Parry.¹¹ More recently, Checco *et al* employ chemically nanopatterned surfaces as templates for the condensation of nanometer-sized liquid drops of ethanol.⁸ The experimental results show clearly that condensed nanoliquids can be controlled through the vapor phase and that their shape can be measured in situ using noninvasive scanning probe techniques.

As put forward in Ref. 12, wedge wetting represents an interesting physical problem in itself, in addition to serving as a prelude to the study of wetting of corrugated surfaces. In this philosophy, in the present work we study the adsorption of helium in alkali wedges at zero temperature within a fully unrestricted density-functional theory (DFT) as described in the following sections.

2. Classical theories of adsorption in corners

In this section we review the main approaches applied to the description of the various meniscus shapes of a liquid adsorbed in a linear wedge with aperture on the (x, z) plane and in the thermodynamic limit in the y direction, $L_y \rightarrow \infty$, along with the possible shape transitions that may take place as one changes the wedge aperture, the vapor pressure or the equilibrium temperature.

Within classical theories of wetting phenomena on planar surfaces, simple thermodynamics arguments show that by changing the state of a liquidlike layer on a substrate in a specifically chosen way, it is possible to provoke unlimited growth of the thickness l , giving rise to a wetting phase transition. If the growth takes place a) by approaching the liquid-vapor coexistence curve from the vapor side it is called complete wetting, b) by changing the state of the fluid along the coexistence line towards the wetting temperature T_w is it known as critical wetting if the growth is continuous, or first-order wetting if the height l of the film changes discontinuously to a macroscopic value. At given temperature T , Young's equation gives the contact angle $\theta(T)$ at the triple line of a macroscopic drop

$$\cos \theta(T) = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \quad (1)$$

with v, l, s respectively denoting the vapor, liquid and solid phases and with $\sigma_{ij}(T)$ the surface tension at the ij interface. The transition is first order or continuous depending on the manner on which $\cos \theta$ approaches unity as $T \rightarrow T_w$; if $\partial \cos \theta / \partial T \rightarrow \text{const} > 0$ the transition is first order, and continuous if the constant vanishes.

Now if one considers a linear wedge with aperture 2φ exposed to vapor below saturation, i.e., at a chemical potential $\mu = \mu_0 + \Delta\mu < \mu_0$, it has been shown by macroscopic, thermodynamic reasoning,¹² regarding both equilibrium and stability conditions, that the resulting configurations are unique and stable *iff* $\theta + \varphi < \pi/2$. If $\theta + \varphi > \pi/2$, no macroscopically stable adsorbate is possible. With varying T at fixed $\Delta\mu$, a macroscopic adsorbate appears in the well when

$$\theta(T, \Delta\mu) = \pi/2 - \varphi \quad (2)$$

then in a wedge, the wetting transition at coexistence is shifted to $T_\varphi < T_w$ such that

$$\theta(T_\varphi, 0) = \pi/2 - \varphi \quad (3)$$

Such a discontinuous change in behavior as $|\theta - \pi/2| = \varphi$ has been corroborated in microgravity experiments.¹³

Note that Eq. (2) is not restricted to coexistence. For $\varphi < \pi/2$, $T = T_\varphi(\Delta\mu)$ is the locus of a continuous wetting transition for $\Delta\mu < 0$, that becomes very similar to capillary condensation in the narrow wedge limit $\varphi \rightarrow 0$. An important limitation is neglect of gravity, which is a valid approximation provided that all relevant lengths are small compared to the capillary length $a_c = (\sigma_{lv}/m\rho_0g)^{1/2}$ at bulk density ρ_0 .

More formally, the shape of equilibrium film-vapor interface configurations can be determined by minimizing the total thermodynamic potential Ω that includes the cost in free energy to distort a flat interface into a curved meniscus. For a finite fluid system, the grandpotential functional decomposes into a bulk Ω_b , a surface Ω_s and a line Ω_l contribution, which depend on different characteristics of the density configuration as follows:

a) The bulk contribution depends only on the bulk densities of liquid and vapor, whose equilibrium values $\bar{\rho}_l, \bar{\rho}_v$ minimize Ω_b .

b) The surface contribution is identical to the surface free energy of the corresponding flat substrate and depends on the asymptotic layer thickness l and –parametrically– on the liquid and vapor densities $\bar{\rho}_l, \bar{\rho}_v$ at equilibrium. The actual width \bar{l} minimizes Ω_s , thus T_w and other wetting properties of the system are fixed by the surface free energy.

c) Only Ω_l depends on the interfacial profile $z(x)$ and –parametrically– on l and the densities. The condition $\delta\Omega_l/\delta z(x) = 0$ at the equilibrium values of thickness and densities gives the equilibrium profile.

Usually, one searches to minimize the difference $\Delta\Omega = \Omega - \Omega_0$ between surface–plus–line grandpotentials (per unit length) of the wedge filled with liquid with re-

spect to that filled with vapor, with the general form.

$$\Delta\Omega = \int_0^L dx \varepsilon[x, z(x)] - (\mu_l - \mu_v) n \quad (4)$$

The various descriptions offered in the literature consider either a fixed number of fluid particles per unit length $n = N/L$

$$n = \rho_0 \int_0^L dx [z(x) - |x| \cot\varphi] \quad (5)$$

at saturation pressure¹ or a fixed volume V .³ Models also differ in the specific choice of the energy density kernel in Eq. (4); the latter always contains the curvature energy ε_c ,

$$\varepsilon_c = \sigma_{lv} (1 + z_x^2)^{1/2} \quad (6)$$

but while the more phenomenological approaches resort to the empirical surface tensions to introduce the surface contribution to the functional, the so-called effective Hamiltonian model includes a substrate-atom interaction to represent more accurately the influence of the external confining field.³ This viewpoint is similar to the earlier proposal for the liquid profile of a wetting liquid in a corner put forward in Ref. 1. In the first case, the equilibrium shape of a nonwetting liquid can be analytically computed and shown to correspond to a circle with radius $R = \sigma_{lg}/(\rho_0 \mu_l)$ that intersects the walls at θ , located at a finite height $(0, z_c)$. If $\frac{\pi}{2} + \varphi \geq \theta > \frac{\pi}{2} - \varphi$, the meniscus is convex, and concave for $\theta < \frac{\pi}{2} - \varphi$. A planar meniscus indicative of a wedge filling transition appears when $\theta = \frac{\pi}{2} - \varphi$. Moreover, a spherical bridge that intersects the walls at the contact angle θ can exist *iff* $z_c > R$, implying $\theta > \pi/2 + \varphi$. This rigorous geometrical outcome strictly coincides with the more phenomenological description attained by means of thermodynamical arguments.¹²

3. Density functional description of wedge wetting

Recently, we have presented the first complete calculation of the structure of liquid ⁴He confined to a concave nanoscopic wedge with alkaline walls, as a function of the opening angle of the walls, within a finite-range density functional formalism.¹⁴ For a translationally invariant system along the y -direction, the equilibrium density profile $\rho(x, z)$ of the helium atoms depends on the (x, z) coordinates only. We compute the density profile that minimizes the zero temperature grandpotential $\Omega = E - \mu N$, with N the grandcanonical ensemble average of the particle number operator,

$$N = \int d^3\mathbf{r} \rho(\mathbf{r}) \equiv L \int \int dx dz \rho(x, z) \quad (7)$$

The variation $\delta\Omega/\delta\rho$ gives rise to the integrodifferential Euler-Lagrange equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\rho) + V_s(x, z) \right] \sqrt{\rho(x, z)} = \mu \sqrt{\rho(x, z)} \quad (8)$$

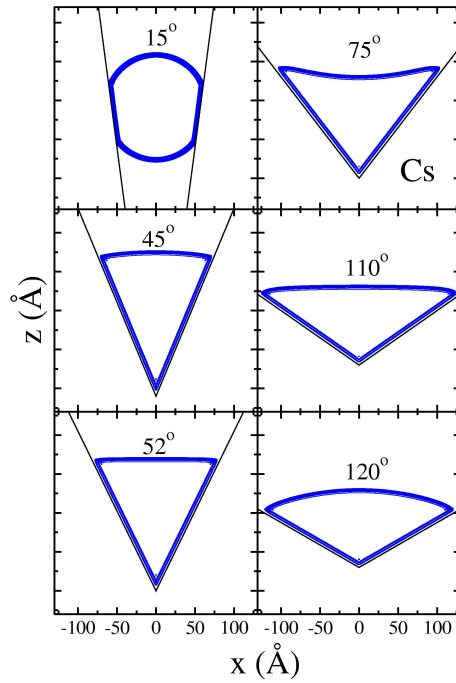


Fig. 1. Density profiles of helium at $n = 280 \text{ \AA}^{-1}$ in a Cs corner for several angular openings. The distance between major tick marks on the z axis is 50 \AA . The center of the 15° configuration is about 400 \AA above the apex of the wedge. Equidensity lines are drawn from $\rho = 0.9\rho_0$ to $0.1\rho_0$ in steps of $0.1\rho_0$.

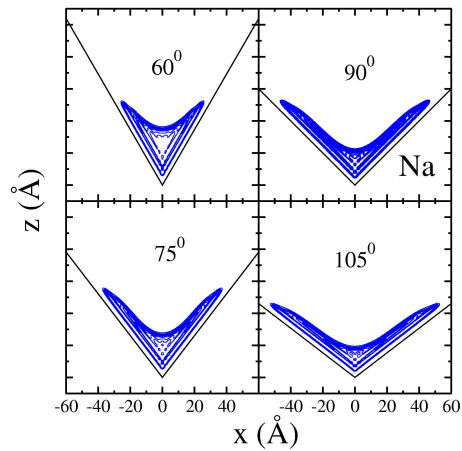


Fig. 2. Density profiles of helium at $n = 15 \text{ \AA}^{-1}$ in a Na corner for several angular openings. The distance between major tick marks on the z axis is 20 \AA . Equidensity lines as in Fig. 1

with $V(\rho)$ the effective potential constructed as the first functional derivative of the potential energy density per unit length, and with $V_s(x, z)$ the confining field. In

Ref. 14, we have selected the full Orsay-Trento (OT) DF.¹⁵ We have also chosen to approximate $V_s(x, z)$ by the summation of two planar potentials, each of the form given in Ref. 16, at an angle 2φ . Double-counting effects are unimportant for values of 2φ below 120° , far from the wedge apex and for the fairly high linear densities here considered. Equation (8) is solved by an imaginary time method and employing a Fast Fourier Transform algorithm to generate the convolution terms in $V(\rho)$ from the atom density $\rho(x, z)$.

We illustrate the main results of our calculation for the cases of cesium and sodium, which are respectively not wetted and wetted by ^4He at zero temperature. In either case, we first compute a sequence of pancake-shaped systems on the corresponding flat surface characterized by the linear density $n = N/L$. The chemical potential of the helium particles as a function of n asymptotically approaches the bulk figure $\mu_0 = -7.15$ K in the case of Cs, and the prewetting chemical potential $\mu_{pw} = -8.75$ K for Na. Up to linear densities of several hundreds \AA^{-1} , the density profiles of the bars confirm the nanoscopic spatial scale of the systems.

Typical shape profiles for helium at various apertures 2φ are shown in Fig. 1 for a Cs wedge with a linear ^4He density of 280\AA^{-1} , and in Fig. 2 for Na walls with $n = 15 \text{\AA}^{-1}$. Starting from a convex pancake on a flat Cs surface and decreasing the opening, one can generate a sequence of changes with the following landmarks: a) a filling transition where the meniscus curvature vanishes takes place for an opening near 110° , b) a concave meniscus appears for smaller angles, that persists within a large angular interval; c) an ‘emptying’ transition happens, near 52° , where the meniscus becomes planar; d) the convex shape reappears for even smaller angles; e) a bridge is formed, that will be expelled from the wedge for sufficiently narrow apertures. It should be kept in mind that in our philosophy, the term ‘transition’ does not refer to a thermodynamic phase transition, but to a crossover between two different regimes characterized by geometry and energetics. The bridge profiles are perfectly circular, in agreement with classical theories of the preceding Section. By contrast, in Fig. 2 we appreciate the spread of a wetting liquid in a strongly attractive Na corner, with a rather deep concave meniscus at all angles above $2\varphi_F \approx 30^\circ$. An emptying transition takes place at $2\varphi_F$, after which, the sample evolves into a nanoscopic bridge.

The above shape sequences are in strict correspondence with energetics as a function of the wedge opening and of linear density. Figure 3 shows the chemical potential of helium atoms in a Cs wedge parametrized by $n = 70, 140$ and 280\AA^{-1} . We see that the three curves cross at the bulk value μ_0 for the filling angle $2\varphi_F = 110^\circ$ and for the emptying one $2\varphi_E = 52^\circ$. Between these openings the chemical potential μ lies below the bulk value μ_0 with positive derivative $d\mu/dn$, thus the corresponding wedge configurations are stable. Instead, both above the filling angle φ_F and below the emptying one φ_E , μ lies above its thermodynamic limit with negative $d\mu/dn$, thus corresponding to metastable systems. These characteristics are confirmed by the behavior of the grandpotential per unit length $\Omega/L = E/L - \mu n$, where E/L is the energy per unit length; at φ_F , Ω/L is independent of n and

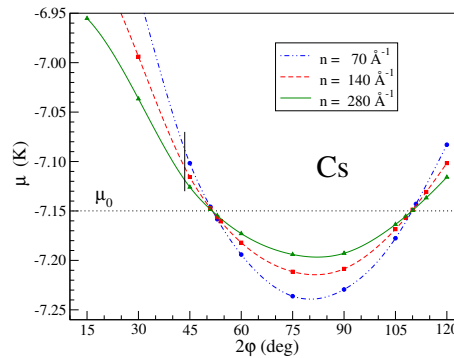


Fig. 3. Chemical potential of helium atoms in a Cs wedge as a function of angular opening 2φ for linear densities 70, 140 and 280 \AA^{-1} . Wedge configurations to the left of the vertical segment near 43° have higher energies than a flat pancake with the same linear density.

vanishes for these large nanoscopic amounts of fluid. Accordingly, these helium samples undergo the kind of filling transition derived for macroscopic systems.³ In Ref. 14 we have proposed an effective way of determining the contact angle θ of ^4He on Cs by means of DF calculations, looking for the value of $2\varphi_F \sim 110^\circ$ where the grandpotential is independent of n . This procedure gives a contact angle $\theta = \pi/2 - \varphi_F = 35^\circ$ for ^4He on Cs, in agreement with experimental evidence and earlier theoretical, DF-based, estimates.^{17,18}

For the stable configurations in the range $[\varphi_E, \varphi_F]$, the disappearance of the solid-vacuum interface at the meniscus contact line, leaving only a liquid-vacuum interface at the free surface, is the source of the energy gain. Instead, as φ becomes smaller than φ_E , the system shifts to a nonwetting regime; in this case, it is energetically favorable to hold vacuum, rather than liquid, near the apex. Consequently, an inner convex meniscus appears away from the corner, forming a bridge with increased energy.

It is interesting to note that within the interval $[\varphi_E, \varphi_F]$, two stable profiles exist for each coverage; in particular, this is the case for the flat menisci configurations at $\mu = \mu_0$. This is a genuine finite size effect intrinsic to the current nanoscopic samples, since in macroscopic systems only a filling transition is expected, according to the classical theories in Section 2. In fact, in the truly macroscopic regime, all equilibrium configurations take the bulk values, *i.e.*, chemical potential and saturation density, regardless the wedge opening.

The mechanism of condensation is better understood examining the adsorption isotherms $\mu(n)$ in a wedge with fixed aperture. No condensation can take place in the wedge for openings below φ_E , since the ^4He configurations in the wedge are always metastable with respect to the bulk. For all angles in the stable domain, condensation takes place with a jump in the linear density from $n = 0$ to a finite value n_F . By using the Maxwell construction (or, equivalently, by identifying the crossing between the $\mu(n)$ and E/N curves) one can identify the chemical potential

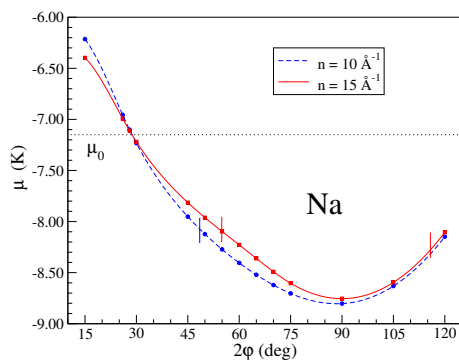


Fig. 4. Chemical potential of helium atoms in a Na wedge as a function of angular opening 2φ for linear densities $n = 10$ and 15 \AA^{-1} . For $n = 15 \text{ \AA}^{-1}$, wedge configurations within the vertical segments are stable with respect to the infinite pancake configuration. For $n = 10 \text{ \AA}^{-1}$, wedge configurations to the right of the corresponding vertical segment are stable with respect to the infinite pancake configuration.

and density at the corresponding jump. This is indicated in Fig. 5, where we show the size of the "pre-filling/pre-emptying" jump in density as a function of angle for a Cs wedge (circles) together with the corresponding chemical potential (squares). We realize that n_F diverges at the filling and emptying transitions and encounters a shallow minimum around 2.4 \AA^{-1} at $2\varphi = 90^\circ$. Correspondingly, the chemical potential at the jump displays a minimum of about -7.5 K . In the strong Na adsorber, only the divergence at the emptying opening shows up; starting from large angles, the jump density n_F decreases monotonically from the planar prewetting value near 0.14 \AA^{-1} (per unit perpendicular length) to a minimum around 0.11 \AA^{-1} . In either case, we have found that for the linear densities under consideration helium bridges are metastable (i.e. have higher energies) with respect to helium pancakes deposited on planar surfaces. These limits are shown in Figs. 3 and 4 by vertical segments. Similarly, Cs wedges corresponding to openings $2\varphi > 120^\circ$ are metastable with respect to pancakes with the same number of atoms. In these metastability regions the pancake, which is a symmetry breaking configuration, is energetically favored with respect to the axially symmetric configuration.

We stress that one of the most important, newest features of the results here presented is precisely the occurrence of an 'emptying' transition and the formation of metastable bridges. This is not expected on the basis of macroscopic thermodynamic arguments, and even seems to contradict the expectation that a narrow wedge should behave as a small pore or slit and be filled by capillary condensation (CC) below SVP. In fact, the latter is the behavior to be expected for sufficiently large helium samples. For the nanoscopic amounts of material here considered, bridges formed between two parallel plates destabilize as the distance between walls overcomes some critical value.¹⁹ This is largely a nontrivial effect, in view of recent experimental evidence on the formation of helium-void micropuddles on rough Cs surfaces.²⁰

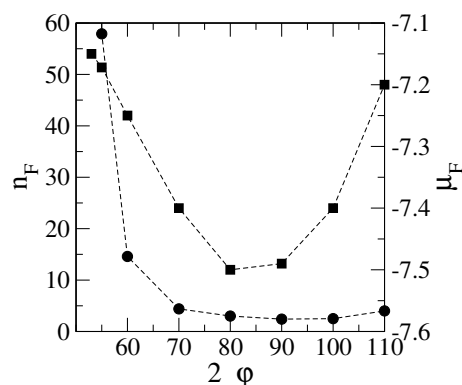


Fig. 5. Prefiling jump n_F in linear density (circles) and corresponding chemical potential μ_F (squares) as obtained from the adsorption isotherms of helium on Cs wedges as functions of wedge opening (in degrees). The lines are drawn to guide the eye. The divergence at an angle slightly above 110° is not shown.

4. Summary

In the first detailed, fully unrestricted, DFT calculation of the structure and energetics of nanoscopic samples of ^4He in alkali linear wedges at zero temperature, we have found a sequence of shapes that includes one filling transition on the non-wettable Cs, and a threshold for metastable configurations where helium does not populate the wedge apex. Condensation at negative grandpotential, accompanied by pre-filling jumps in the linear density, takes place for angles above threshold –and below the filling aperture in the case of Cs– in any alkaline wedge. When the helium fluid is near saturation, the angle for the filling transition is stable against changes in the linear density and can be identified with the contact angle on a planar substrate. We have found that metastable configurations appear for finite average numbers of ^4He atoms per unit length; it is important to keep in mind that a droplet with finite atom number N on Cs is metastable, not only with respect to bulk, but also with respect to a thin film at finite coverage N/A . Inspired by recent experiments on physisorption on nanostructured substrates, we suggest that deposition of *finite*, nanoscopic amounts of helium on alkali wedges, could lead to actual confirmation of our current predictions.

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