Extraordinary wetting phase diagram for mixtures of Bose-Einstein condensates

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The possibility of wetting phase transitions in Bose-Einstein condensed gases is predicted on the basis of Gross-Pitaevskii theory. The surface of a binary mixture of Bose-Einstein condensates can undergo a first-order wetting phase transition upon varying the interparticle interactions, e.g., Feshbach resonances. Interesting ultralow-temperature effects shape the wetting phase diagram. The prewetting transition is, contrary to general expectations, not of first order but critical, and the prewetting line does not meet the bulk phase coexistence line tangentially. Experimental verification of these extraordinary results is called for, especially now that it has become possible, using optical methods, to realize a planar "hard wall" boundary for the condensates.

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In this Letter we pose and answer theoretically the following fundamental questions. Is there a wetting phase transition possible in ultra-cold dilute gases which undergo Bose-Einstein condensation (BEC)? How many species of atoms are needed to compose two coexisting phases with an interface? What is the nature of the surface or “wall” at which these phases are “adsorbed”? If a wetting phase transition occurs, is its character first-order or critical? What is the nature of possible prewetting phenomena away from bulk two-phase coexistence? We focus on the essential physics in the application of wetting theory to BEC and give details of the calculations elsewhere.

The simplest system, a one-component gas, is insufficient for studying wetting transitions, because the condensate fraction and the normal fraction are fully mixed in position space. Spatial segregation is only possible in an external potential (e.g., gravity). Without this potential an interface between normal fraction and condensate does not exist, and therefore the essential interfacial tension is missing.

The next simplest BEC system is a two-component gas. Binary mixtures of trapped BE condensates of alkali-metal atoms have received much attention, experimentally and theoretically, since the seminal predictions concerning their phase behavior by Ho and Shenoy. Different degrees of spatial segregation of two pure-component condensates at two-phase coexistence, and the possibility of a symmetric-asymmetric configurational transition in a trap, have been elucidated by Ao and Chui and Svidzinsky and Chui.

We exploit these findings in the context of wetting phenomena, and point out the existence of a surface phase transition from partial to complete wetting, upon varying the intra- or inter-species interactions in mixtures of BE condensates. The surface consists of a planar “hard wall”, at which the condensate wave functions vanish.

The basic physics of wetting is best indicated by invoking the familiar energy balance known as Young’s law,

$$\gamma_{w1} = \gamma_{w2} + \gamma_{12} \cos \theta \quad (1)$$

where $\gamma_{wi}$ is the surface (free) energy of a phase of pure component $i$, $\gamma_{12}$ is the interfacial tension between pure phases 1 and 2, and $\theta$ is the contact angle with which the 1-2 interface meets the surface. One of the components, say 2, is preferentially adsorbed at the surface, so that $\gamma_{w1} > \gamma_{w2}$. The surface phase transition from partial wetting ($\theta > 0$; Figure 1a) to complete wetting ($\theta = 0$; Figure 1b) is then the dramatic phenomenon in which, at the surface, pure phase 1 is displaced by a macroscopically thick wetting layer of pure phase 2. Thus, the W1 surface is replaced by a W2 surface in parallel with a 1-2 interface.

The physical implications of the singularity structure around wetting transitions have been the subject of impressive experimental, theoretical, and simulational research.

In view of the ultra-low (typically nanoKelvin) temperature needed for BEC in dilute gases, the quantum mechanical many-body theory at $T = 0$ is appropriate. For weakly interacting gases the Bogoliubov mean-field theory of BEC is justified. For our inhomogeneous binary mixture one obtains two coupled Gross-Pitaevskii (GP) equations for the condensate order parameters $\psi_1 = F_1 e^{i\chi_1}$ and $\psi_2 = F_2 e^{i\chi_2}$. We recall that $\psi$ is the ground state expectation value of the Boson field operator. It can be chosen real here, since stationary (non-flowing) condensates are assumed, so $\chi_1 = \chi_2 = 0$. 

![Partial wetting](a) Complete wetting. A macroscopic layer of condensate 2 intrudes between the wall and condensate 1.

![Complete wetting](b) Complete wetting. A macroscopic layer of condensate 2 intrudes between the wall and condensate 1.

FIG. 1: a) Partial wetting. The interface between the two condensates makes a finite contact angle with the wall. b) Complete wetting. A macroscopic layer of condensate 2 intrudes between the wall and condensate 1.
We adopt the standard geometry for wetting and confine the atoms to the half-space \( z > 0 \). The relevant surface is the \( z = 0 \) plane. It is then natural to employ the grand canonical ensemble, with chemical potentials \( \mu_1 \) and \( \mu_2 \). The GP equations are the Euler-Lagrange equations of the grand potential functional

\[
\Omega[\psi_1, \psi_2] = \int_{z \geq 0} dr \left( \sum_{i=1,2} \left( \frac{\hbar^2}{2m_i} \nabla^2 - \mu_i \right) \psi_i(r) + \frac{G_{ii}}{2} |\psi_i(r)|^4 \right) + G_{12} |\psi_1(r)|^2 |\psi_2(r)|^2
\]

(2)

The sum is over the two species, with atomic masses \( m_i \). The repulsive interactions \( G_{ij} \) are related to the s-wave scattering lengths \( a_{ij} \) through \( G_{ii} = 4\pi\hbar^2 a_{ii}/m_i \) for like particles and \( G_{12} = 4\pi\hbar^2 a_{12}(1/m_1 + 1/m_2) \) for unlike particles. For alkali-metal atoms, \( a \approx 10^{-8} \AA \).

The confining potential is taken to be a hard wall at \( z = 0 \), so that

\[
\psi_1(x, y, 0) = \psi_2(x, y, 0) = 0
\]

(3)

The closest experimentalists have come to make a hard wall is to use an evanescent wave, blue-detuned, extending from within a planar prism. The turn-on distance of this optical wall is typically only about \( \lambda/2\pi \approx 80 \text{nm} \). To contain the atoms, a conventional quadratic-confining magnetic trap can be added, so that a "quasi-square" exponential potential results for \( z < 0 \), and the usual \( a \xi^2 + b y^2 + c z^2 \) for \( z > 0 \). In order for volume forces due to a non-uniform external potential to be negligible compared to surface forces governing wetting, the harmonic potential must be sufficiently flat-bottomed near \( r = 0 \). For a characteristic length of the order of microns or longer we can ignore the harmonic potential in the calculations and assume translational invariance of \( \psi \) in \( x \) and \( y \) directions.

The known condition for bulk phase separation of the binary mixture is that the unlike particles repel each other more strongly than the like ones on average, \( K = G_{12}/\sqrt{G_{11} G_{22}} > 1 \). Otherwise, a single mixed phase results. Bulk phase coexistence requires equal pressure, \( P_1 = P_2 \), in the two phases, with \( P_i = \mu_i/2G_{ii} \). A bulk triple point with coexisting mixed and pure phases 1 and 2 is found for \( K = 1 \). This triple point bears a resemblance to a critical point in that the interfacial tension between pure phases 1 and 2 vanishes. However, the phases themselves remain distinct.

The bulk condensate number densities in the pure phases are \( \rho_i = |\psi_i(\infty)|^2 = \mu_i/G_{ii} \). A "healing length" \( \xi_i = \hbar/\sqrt{2m_i \rho_i G_{ii}} \) characterizes the recovery distance of the order parameter from a disturbance, e.g., a surface where \( \rho = 0 \). A typical value is \( \xi \approx 10^{-13} \AA \). The two surface grand potentials \( \gamma_{wi} \) are proportional to the product of the pressure and this healing length, \( \gamma_{wi} = (4\pi\sqrt{2}/3)P\xi_i \), which defines a surface "thickness". For strongly repulsive interactions and/or high densities, the healing length of a condensate is short, and its surface tension is low, so that it prefers to be near the surface. This suggests to define a "surface field" proportional to the difference \( \xi_1 - \xi_2 \).

The second important length is the "penetration depth" \( \Lambda \), characterizing the distance over which one condensate decays or "penetrates" into the other at the 1-2 interface. \( \Lambda_i = \xi_i/\sqrt{K - 1} \). A typical value is \( \Lambda \approx 1 \mu m \). This length diverges when approaching the triple point. Ao and Chui discuss the following two limits for which we determine the wetting behavior.

A) Strong segregation limit: Partial Wetting

In the limit \( \Lambda \ll \xi \) or \( K \to 1 \) the condensates show almost no mutual penetration. The interface then consists of two surfaces, one where condensate 1 decays to zero over the healing length \( \xi_1 \), and an adjacent one where condensate 2 vanishes over \( \xi_2 \). The interface thickness is thus \( \xi_1 + \xi_2 \) and its tension is approximately \( \gamma_{12} \approx \gamma_{w1} + \gamma_{w2} \). There can be no complete wetting, since the energy cost of an interface is too high to be able to satisfy Young’s law with \( \theta = 0 \).

B) Weak segregation limit: Complete Wetting

In the experimentally more relevant limit \( \Lambda \gg \xi \) or \( K \to 0 \) the mutual penetration of the condensates leads to mixing on the scale of \( \Lambda_1 + \Lambda_2 \). In spite of its huge thickness, the interface has a low tension, since the energy per unit volume scales as \( \gamma_{wi}/(\Lambda/\xi)^2P \). As a result, \( \gamma_{12} \propto P(\xi_1 + \xi_2)/\sqrt{K - 1} \). The interfacial tension vanishes at the triple point with a square-root singularity. For Young’s contact angle we obtain

\[
\cos \theta = \text{const.} \left( \frac{\xi_1 - \xi_2}{\xi_1 + \xi_2} \right) (K - 1)^{-1/2}
\]

(4)

This implies that a wetting transition is unavoidable upon approach of the triple point. Indeed, the wetting phase boundary implied by \( \Box \) is given by

\[
(\xi_1/\xi_2 - 1) \propto (K - 1)^{1/2}
\]

(5)

A full numerical computation corroborates the physical insights gained so far, and leads to the wetting phase diagram at bulk two-phase coexistence shown in Fig.2. The wetting transition is of first order. On the phase boundary the grand potential of partial wetting crosses that of complete wetting, and both states have metastable continuations. Interestingly, at the wetting transition the grand potential is degenerate: all wetting layers have the same energy, regardless of the layer thickness. This is akin to what happens at the wetting transition in an Ising model at \( T = 0 \), where the interface consists of a plane of broken bonds at an arbitrary distance from the surface. The usual entropic repulsion between the surface and the interface due to interfacial capillary wave fluctuations is absent at \( T = 0 \).

Yet, in contrast with Ising spins on a lattice, the continuum field theory we are dealing with allows one to “inflate” a wetting layer by varying its shape and thickness continuously between infinitesimal and macroscopic...
There are two premises in the general reasoning, which are not fulfilled here. Firstly, at this first-order wetting transition there is no abrupt jump of the film thickness between a microscopic and a macroscopic value, but all intermediate values are equally stable due to the grand potential degeneracy. Since there is
no interface potential barrier, for consistency the prewetting transition must be continuous instead of first-order, and we find that it is. Secondly, since this prewetting transition is a second-order nucleation transition, unlike for ordinary prewetting, the difference in adsorption on either side of the transition does not diverge upon approach of the wetting transition at $W$, and the condition for a tangential meeting is not met. Consistently, we find an intersection at a finite angle.

Within the wetting phenomenology we reinterpret the interesting symmetric-asymmetric (SA) transitions predicted for an axially symmetric square-well trap, and for a conventional quadratic magnetic trap. In the symmetric (S) state the condensates form concentric clouds. This corresponds to complete wetting (Fig.1b), with, e.g., a W2 surface and an embedded 1-2 interface in a “cherry” configuration. This state may exchange stability with one (A) which breaks the trap symmetry, with a planar 1-2 interface cutting across the system. This is partial wetting (Fig.1a).

For a square-well trap, a surface energy balance determines the SA transition. However, it is not governed by Young’s law, but by finite-size effects, cylindrical geometry and particle number conservation. Consequently, the contact angle at the SA transition does not tend to zero continuously as in the \textit{bona fide} wetting transition. Instead, it jumps from a finite value $\theta_{SA}$ to zero. For a quadratic trap, surface and volume contributions are entangled in the energy balance. In the S state the component with the largest self-repulsion is on the outside. For sufficiently small trap radius, an A state is favored, to relieve the high capillary pressure across the curved 1-2 interface in the S state. The wetting interpretation is complicated here due to the spatially varying external potential and the absence of an articulated surface.

In conclusion, in view of the extraordinary ultralow-temperature effects in the predicted wetting phase diagram for binary mixtures of Bose-Einstein condensed gases, we advocate an experimental study of wetting and prewetting in a trap which is suitable for observing true wetting singularities. The confinement should consist of a half-space with one planar “hard wall”, i.e., a steep repulsion with a turn-on length smaller than the healing lengths and penetration depths of the condensates. A mild conventional trap may be used to keep the gas near the wall. The wetting transitions can be induced by tuning the interatomic scattering lengths using Feshbach resonances.

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