Dimers in Two-Dimensional ^{3}He-^{4}He Mixtures

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Ground-state properties of two-dimensional ^{3}He-^{4}He mixtures are studied at zero temperature. A general argument based on the long-ranged attraction of the phonon exchange is given for the existence of ^{3}He dimers in low-concentration mixtures with ^{4}He. The binding energy of dimers ranges from milli- to microkelvins with increasing ^{4}He density. By comparing the ^{3}He impurity chemical potential in ^{4}He with the one in pure ^{3}He we conclude that at finite pressures ^{3}He dimers form a mixture with ^{4}He with a maximum solubility of ≈3%.

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The first superfluid layer of a ^{4}He film on a smooth substrate forms a nearly two-dimensional (2D) self-bound liquid. At very low densities and absolute zero temperature, the homogeneous liquid condenses into patches surrounded by gas or vacuum. At high densities the liquid either solidifies or a second atomic layer begins to form, depending on the strength of the substrate potential. ^{3}He atoms in two dimensions form a gas in the density range of interest in this paper, although the interaction between two atoms is sufficiently attractive to bind *isolated* pairs of ^{3}He atoms with opposite spins with an energy of about 20 μK. Atomic monolayers of ^{3}He and ^{4}He mixtures can be realized in strongly attractive substrates and they form a quasi-two-dimensional mixture [1], but low temperature experiments have left room for speculations on the quantum nature of the ^{3}He component in the mixture. Over the years homogeneous atomic mixing at finite pressure [2], Cooper pairing [3], dimer formation [4], and phase separation into self-bound 2D Fermi liquid [5] have been suggested.

We present in this work a careful theoretical analysis of the phase diagram of two-dimensional, low concentration ^{3}He-^{4}He mixtures. We evaluate the effective ^{3}He-^{3}He interaction and show that the long-ranged attraction induced by phonon exchange is, in the dilute limit, sufficient to bind ^{3}He dimers. We also give an estimate of the maximum solubility by comparing our calculated chemical potentials with recent Monte Carlo results for the pure 2D ^{3}He gas. We use the variational approach based on the Jastrow-Feenberg ansatz for the wave function [6,7] *plus* correlated basis functions (CBF) perturbation theory to infinite order. The method gives accurate results for helium fluids both in two and three dimensions.

The scattering equation for two ^{3}He impurities with opposite spins in liquid ^{4}He can be written in the form of a Schrödinger equation,

$$\left[-\frac{\hbar^2}{m_3}\nabla^2 + V_{\mathrm{scat}}(r) - E_b\right]\phi(\mathbf{r}) = 0\,, \qquad (1)$$

where m_3 is the bare ^{3}He mass and $V_{\mathrm{scat}}(r) \equiv V(r) + w_{\mathrm{ind}}(r) + \Delta V_e(r)$ is the effective potential. The first term is the bare interaction [8] and the second term is the phonon-induced interaction. $\Delta V_e(r)$ is a quantitatively important contribution coming from higher order correlations and "elementary diagrams" [7]. The quantities entering the effective interaction are accurately known from the properties of pure ^{4}He and one ^{3}He impurity in ^{4}He; however, a number of exact statements can be made that do not rely on the quality of generically approximate methods.

The longest-ranged part of the interaction comes from the phonon-induced interaction $w_{\mathrm{ind}}(r)$ which can be expressed in momentum space in terms of the ^{4}He-^{4}He and ^{3}He-^{4}He structure functions, $S^{(44)}(k)$ and $S^{(34)}(k)$:

$$\tilde{w}_{\mathrm{ind}}(k) = -\frac{1}{2}\frac{[S^{(34)}(k)]^2}{S^{(44)}(k)}\left[\frac{\hbar^2k^2}{m_3} + \frac{\hbar^2k^2}{2m_4S^{(44)}(k)}\right]. \qquad (2)$$

The long-wavelength expansion of the phonon-induced potential $\tilde{w}_{\mathrm{ind}}(k)$ is

$$\tilde{w}_{\mathrm{ind}}(k) = -\beta^2 m_4 c^2 + \mathrm{const} \times k^2 - \frac{\hbar^3\beta^2 m_4}{4m_3^3 c}k^3 + \mathcal{O}[k^4] \quad \text{as } k \to 0+\,. \qquad (3)$$

Here $\beta = S^{(34)}(0+)$ is the volume excess factor of ^{3}He atoms introduced in Ref. [9], c is the speed of sound, and m_4 and m_3 are the masses of helium isotopes. The first odd power in the above expansion is k^3; this power determines the longest-ranged part of the interaction,

$$w_{\mathrm{ind}}(r) = -\frac{9\hbar^3\beta^2 m_4}{8\pi\rho m_3^3 c}\frac{1}{r^5} + \mathcal{O}[r^{-6}] \quad \text{as } r \to \infty\,. \qquad (4)$$

Evidently, the longest-ranged part of the effective interaction is attractive. This is, in two dimensions, sufficient [10] for having a bound state of the Schrödinger equation. Hence, the asymptotic form (4) proves that the lowest energy solution of Eq. (1) is a weakly bound state.

The proof of the existence of a dimer mentioned above says nothing about the magnitude of the binding energy and its dependence on the density of the host liquid. In fact, the much shorter-ranged contribution $\Delta V_e(r)$ causes a quantitatively significant increase of the dimer binding energy, which is strongly density dependent as shown in Fig. 1. At zero pressure, which corresponds to the

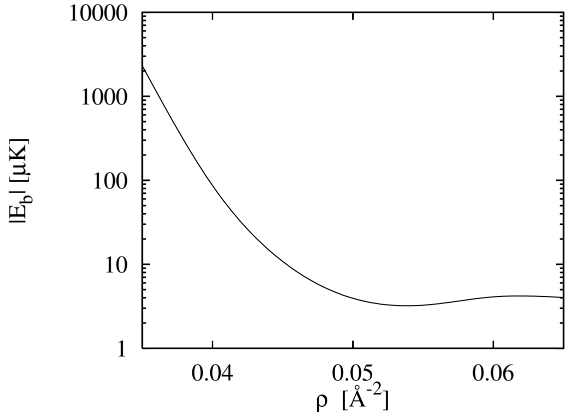

FIG. 1. The binding energy of a dimer of ^{3}He atoms within two-dimensional ^{4}He in logarithmic scale as a function of density.

density $\rho = 0.043$ Å^{-2}, the binding energy is ≈ 26 μK. The binding energy decreases with increasing density; the reason for this is that the attraction of the asymptotic tail of the phonon-induced interaction decreases since the volume excess factor decreases and the speed of sound increases with increasing density. Near the solidification density oscillations of the effective interaction build up; they extend farther and farther out into the tail and also reduce the binding. Since the dimer is very weakly bound, its wave function decays very slowly. Figure 2 shows the wave function for three different densities. They show a maximum at ≈ 4 Å which coincides with the first maximum of the radial distribution function of the pure ^{4}He.

We have shown so far that the dimerized phase is, in the low concentration limit, energetically favorable over the dilute atomic mixture. Next, we need to determine the regime where the dimerized mixture is favored over a phase-separated configuration. In a stable mixture, the chemical potential of the ^{3}He component, $\mu_3^{\text{mix}}(P, x)$, at a given pressure P, must be lower than that of pure ^{3}He at the same pressure; furthermore, $\mu_3^{\text{mix}}(P, x)$ must be an increasing function of concentration.

We start by calculating the ^{3}He chemical potential in the single impurity limit, $\mu_3^I(P)$, and comparing that with Monte Carlo simulation results [11] for pure ^{3}He. The difference between the chemical potentials, $\Delta\mu_3(P) = \mu_3^I(P) - \mu_3^{\text{pure}}(P)$, is shown in Fig. 3 as a function of pressure. At zero pressure the ^{3}He impurity chemical potential is positive, $\approx + 0.13$ K, whereas the chemical potential of the pure ^{3}He gas approaches zero proportional to $\sqrt{P}$. This means that no stable mixture can exist at zero pressure. However, the chemical potential in the pure phase increases faster than for the impurity, and the mixture becomes stable for pressures $P > 0.002$ dyn/cm. The maximum energy difference in the chemical potentials is $\approx - 0.25$ K at $P = 0.1$ dyn/cm. In passing, we note that this energy difference is surprisingly similar to that of the three-dimensional mixture.

The accuracy of our results can be estimated as follows: An upper bound for the impurity chemical potential μ_3^I can be calculated [12] by using the ground-state wave function of $N + 1$ ^{4}He atoms as a trial wave function for the system of N ^{4}He atoms and one ^{3}He impurity:

$$\mu_3^I \leq \left(\frac{m_4}{m_3} - 1\right)\frac{\langle T_4\rangle}{N} + \mu_4\,, \tag{5}$$

where $\langle T_4\rangle$ is the kinetic energy of the ^{4}He component and μ_4 is the chemical potential of the pure ^{4}He. Both quantities can be obtained from simulation data [13] without recourse to semianalytic theories, but of course also within our computational scheme. That way, we can reassure the accuracy of our calculations in two ways: first, by asserting that our estimate from Eq. (5) for the ^{3}He chemical potential agrees sufficiently well with what one would

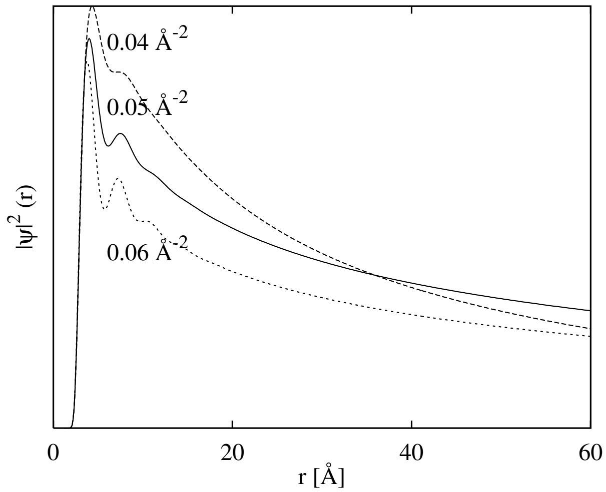

FIG. 2. The square of the ^{3}He wave function for three different ^{4}He densities as marked in the figure.

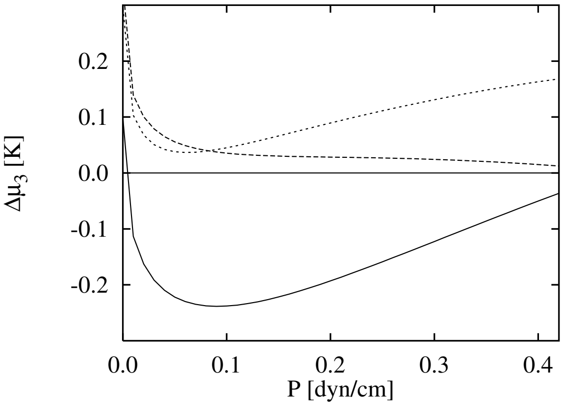

FIG. 3. The difference between the ^{3}He impurity and the pure ^{3}He gas chemical potentials is shown as a function of pressure. The solid line shows the result of the full calculation. The short dashed line is our estimate using Eq. (5), and the long dashed line is the corresponding estimate from Monte Carlo simulations [13] of pure ^{4}He.

obtain from Ref. [13] and, second, the relevant quantity is only the increase of the ^{3}He binding due to improving the wave function, and the energy differences gained by that should be more accurate than the absolute energies.

The estimate (5) yields an upper limit for the impurity chemical potential which is less than 0.1 K above $\mu_3^{\text{pure}}(P)$ for pressure $P > 0.002$ dyn/cm as shown in Fig. 3. Our result for the kinetic energy $\langle T_4 \rangle$ gives a slightly higher upper limit. The difference between our full calculation and the upper limit (5) tells that the gain in energy is about 0.3 K when also the impurity correlation functions are optimized. From that we can conclude that the mixture is stable for pressures $P > 0.002$ dyn/cm and phase separates at very low pressures.

The above analysis applies to the dilute limit. However, both an increasing number of dimers and Fermi statistics screen the pairing interaction at finite ^{3}He concentration, and a homogeneous atomic mixture will eventually form. If such a mixture is stable, we can apply our theory [7] of mixtures. The theory contains optimized Jastrow-Feenberg pair and triplet correlations in all channels and the hypernetted chain summation of diagrams (FHNC-EL), along with corrections within infinite order CBF perturbation theory. In particular, the Euler equations for optimizing the correlations have no solution if the system is unstable against infinitesimal density or concentration fluctuations. Consistent with the fact that we find a dimer state in the zero concentration limit, we find that the homogeneous mixture becomes unstable against infinitesimal concentration fluctuations when the ^{3}He concentration is lowered. We show in Fig. 4 the onset of this instability as a function of density. It is quite tedious to approach the instability because the correlation length diverges at that point, and we must rely on extrapolations from higher concentrations. Two independent calculations give slightly different results: A lower limit of about 1% is found in the FHNC-EL approximation, whereas the more advanced CBF calculations predict a somewhat larger critical concentration of about 3%.

The stability of the mixture requires that the chemical potential must be an increasing function of concentration. For that we need the enthalpy in the mixed phase

$$H(P,x) = \frac{E(P,x)}{N} + \frac{PV(P,x)}{N}, \tag{6}$$

which defines the concentration dependence of the ^{3}He chemical potential at constant pressure,

$$\mu_3(P,x) = H(P,x) + (1-x)\,\frac{\partial H(P,x)}{\partial x}. \tag{7}$$

Here $E(P,x)/N$ is the energy/particle of the mixture and $V(P,x)$ is its volume.

Our results for the concentration dependence of $\mu_3(P,x)$ for three different pressures are shown in Fig. 5. We have subtracted the pure ^{3}He chemical potential in order to highlight the details. The solid lines are the results of our full mixture calculations. The CBF corrections are not visible in the scale of this figure. Short dashed lines leading to the results in the impurity limit are interpolations through the unstable regime as a guide to the eye.

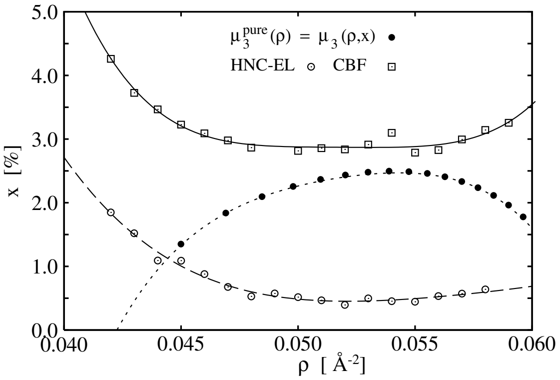

FIG. 4. The figure shows the critical concentrations where the atomic mixture becomes unstable as a function of density. The solid and the long dashed line show the interpolated CBF and FHNC-EL results, respectively; the black dots give the maximum solubility concentrations.

The maximum solubility of ^{3}He into ^{4}He can be determined by comparing the chemical potentials in the mixture and pure ^{3}He gas [14]. Although the calculations for atomic mixtures are not rigorously applicable for the dimerized phase, an interpolation of the chemical potential for finite concentrations and the single-impurity limit can give plausible estimates for the critical concentrations. These can be read off from Fig. 5 as the points where the curves cross the x axis and the results are shown in Fig. 4. The maximum solubility is ≈2.6% at the pressure of 0.1 dyn/cm. It diminishes to zero when $P < 0.002$ dyn/cm as already pointed out, and also near the solidification when $P > 0.5$ dyn/cm. By comparing

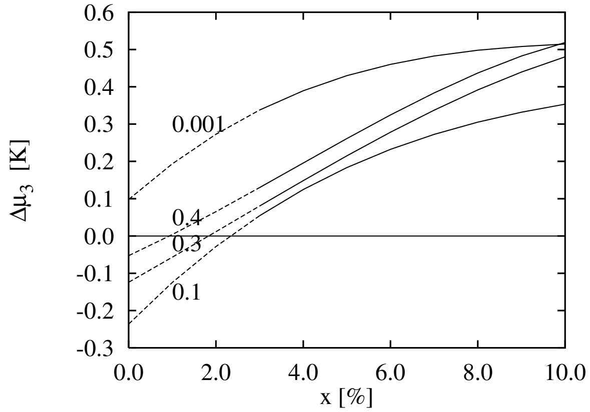

FIG. 5. The difference between the ^{3}He chemical potentials in the mixture and pure ^{3}He gas as a function of concentration at pressures indicated by labels in units [dyn/cm]. The mixture results (full lines) are extrapolated to the impurity results at zero concentration.

the critical concentrations from the global and infinitesimal stability considerations, we conclude that an atomic mixture would be supersaturated and can exist only under favorable experimental conditions. Any little seed can trigger the phase separation as is already well known experimentally in three-dimensional mixtures [14].

Our interpolation between the zero impurity limit and the finite-concentration atomic mixture results show that $\mu_3(P,x)$ is indeed an increasing function of the concentration. This is consistent with qualitative considerations: For a first estimate of the small concentration behavior we may assume that the volume $V(P,x) = \{1 + x[\beta(P) - 1]\}V(P,0)$ is a linear function of concentration and the volume excess factor $\beta(P)$ depends, as in three-dimensional mixtures, only on the pressure. In the two-dimensional fluid, the Fermi energy of the quasiparticles, $E_F = x^2\pi\rho\hbar^2/(2m_3)$, has the same quadratic concentration dependence as the ^{3}He-^{3}He interaction term. Following Ref. [9], we can estimate the interaction term from the volume excess factor and the speed of sound, $E_V = -(\beta - 1)^2 m_4 c^2 x^2/2$. Inserting typical values at zero pressure, $\rho = 0.043$ Å^{-2}, $m_4c^2 = 4.2$ K, and $\beta = 1.5$ from Monte Carlo and our impurity calculations, we find that the quasiparticle Fermi energy is more than a factor of 2 larger than the interaction energy. Thus we conclude that $\mu_3(P,x)$ is an increasing function of concentration indicating a locally stable mixture.

Our analysis of the phases of rigorously two-dimensional ^{3}He should shed some light on the physics of mixture films and on the consequences of dimensionality encountered in these systems. In reality, mixture films are quasi-two-dimensional systems where the motion of the particles into the third dimension is restricted, but not completely suppressed, by a holding potential. The dimer binding energy can be enhanced significantly [15]—compared to the purely two-dimensional phase—if the particles are in an external potential whose width is of the order of the range of the bare interaction. This is the case for realistic atomic monolayers; hence one should reassess the validity of the rigorously two-dimensional approximation. Moreover, adsorbed films show, at sufficiently high surface coverages, the onset of a ripplon excitation [16] which has a much lower energy than the two-dimensional phonon. Ripplon exchange should be particularly relevant for mixture films where the ^{4}He component has more than one atomic monolayer, but where the ^{3}He is still sufficiently dilute to be considered a monolayer. *Both* of these effects *enhance* the dimer binding.

A *reduction* of the dimer binding energy can be expected from Fermi statistics since Eq. (1) should be replaced by the Bethe-Goldstone equation at finite concentrations, and Bashkin's argument [4] on existence of dimers is no longer rigorous. We shall address these issues in further work.

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