Degenerate atom-molecule mixture in a cold Fermi gas

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We show that the atom-molecule mixture formed in a degenerate atomic Fermi gas with interspecies repulsion near a Feshbach resonance, constitutes a peculiar system where the atomic component is almost non-degenerate but quantum degeneracy of molecules is important. We develop a thermodynamic approach for studying this mixture, explain experimental observations and predict optimal conditions for achieving molecular BEC.

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Interactions between particles play a crucial role in the behavior of degenerate quantum gases. For instance, the sign of the effective mean field interaction determines the stability of a large Bose-Einstein condensate (BEC), and the shape of such a condensate in a trap can be significantly altered from its ideal gas form \cite{1}. In degenerate Fermi gases the effects of mean field interactions are usually less pronounced in the size and shape of the trapped cloud, and these quantities are mostly determined by Fermi statistics. The strength of the interactions, however, can be strongly increased by making use of a Feshbach resonance \cite{2}, and then the situation changes.

Recent experiments present two types of measurement of the interaction energy in a degenerate two-component Fermi gas near a Feshbach resonance \cite{3,4,5,6}. At JILA \cite{5} and at MIT \cite{7} the mean field energy was found from the frequency shift of an RF transition for one of the atomic states. The results are consistent with the magnetic field dependence of the scattering length $a$, the energy being positive for $a > 0$ and negative for $a < 0$. In the Duke \cite{3} and ENS \cite{6} experiments with $^{6}$Li, the results are quite different. The interaction energy was obtained from the measurement of the size of an expanding cloud released from the trap. A constant ratio of the interaction to Fermi energy, $E_{\text{int}}/E_{F} \approx -0.3$, was found around resonance, irrespective of the sign of $a$ \cite{4,5}. It was explained in Ref. \cite{4} by claiming a universal behavior in this strongly interacting regime \cite{4}. The ENS studies in a wide range of magnetic fields \cite{6} found that $E_{\text{int}}$ changes to a large positive value when $a$ is tuned positive, but only at a field strongly shifted from resonance.

In contrast to the JILA \cite{5} and MIT \cite{7} studies providing a direct measurement of the mean field interaction energy, the Duke \cite{3} and ENS \cite{6} experiments measure the influence of the interactions on the gas pressure. An interpretation of the ENS experiment involves the creation of weakly bound molecules via three-body recombination at a positive $a$ \cite{6}. Far from resonance, the binding energy of the produced molecules and, hence, their kinetic energy are larger than the trap depth and the molecules escape from the trap. The interaction energy is then determined by the repulsive interaction between atoms and is positive \cite{6}. Close to resonance, the three-body recombination is efficient \cite{4} and the molecules remain trapped as their binding energy $\epsilon_{B}$ is smaller than the trap depth \cite{4,6}. They come to equilibrium with the atoms, reducing the pressure in the system.

Away from resonances, the interaction strength is proportional to $a$, and is given by $g = 4\pi\hbar^{2}a/M$, with $M$ the atom mass. Close to resonance this relation is not valid, as the value of $|a|$ diverges to infinity and the scattering process strongly depends on the collision energy. For Boltzmann gases, already in the 1930’s, Beth and Uhlenbeck \cite{10} calculated the second virial coefficient by including both the scattering and bound states for the relative motion of pairs of atoms \cite{10}. A small interaction-induced change of the pressure in this approach is negative on both sides of the resonance \cite{10}

However, current experiments are not in the Boltzmann regime. In this letter we show that the atom-molecule mixture formed in a cold atomic Fermi gas, constitutes a peculiar system in which the atomic component is almost non-degenerate, whereas quantum degeneracy of the molecules can be very important. This behavior originates from a decrease of the atomic fraction with temperature. It is present even if the initial Fermi gas is strongly degenerate in which case almost all atoms are converted into molecules. We develop a thermodynamic approach for studying this mixture, predict optimal conditions for achieving molecular BEC, and properly describe the interaction effects as observed at ENS \cite{6}.

We assume that fermionic atoms are in equilibrium with weakly bound (bosonic) molecules formed in the recombination process. The molecules are treated as point bosons. Atom-molecule and molecule-molecule interactions are omitted at first, and will be discussed in a later stage. For a large scattering length $a > 0$, the binding energy of the weakly bound molecules is $\epsilon_{B} = \hbar^{2}/(Ma^{2})$, and their size is roughly given by $a/2$. For treating them as point bosons, this size should be smaller than the mean interparticle separation. This requires the inequality $n(a/2)^{3} < 1$, which at densities $n \approx 10^{13}$ cm$^{-3}$ is satisfied for $a < 18000a_{0}$, and excludes a narrow vicinity of the Feshbach resonance.

The presence of molecules reduces the number of particles in the atomic component and to an essential extent...
and can be expected even in the non-superfluid state. The crossover from the BCS to BEC regime \cite{14, 15, 16, 17} is lifted by the interaction between the atoms, which are important for describing a condensed phase of bosons. Dashed curves are obtained including atom-molecule and molecule-molecule interactions.

The molecular chemical potential is negative in the absence of atom-molecule and molecule-molecule interactions. The molecular chemical potential is

\[ \mu_m = \frac{h^2 k^2}{2 M} - \delta |k-k'|/2 \]

where \( \delta = -\text{arctan} q_a \). In the limit of \( q |a| \ll 1 \), Eq. (2) transforms into the ordinary coupling constant \( g = 4 \pi \hbar^2 a / M \).

As we have \( n_1(k, \mu, T) \equiv n_1(k, \mu, T) \equiv \nu_k \), the total energy of the atomic component and the number of particles in this component can be written in the form

\[ E_a = \sum_k \frac{h^2 k^2}{2 M} + \sum_{kk'} \frac{g_{kk'}}{V} \nu_k \nu_{k'}; \quad N_a = 2 \sum_k \nu_k. \]  

In our mean-field approach, the entropy of the atoms is given by the usual combinatorial expression \cite{18}:

\[ S_a = -\sum_k [\nu_k \ln \nu_k + (1 - \nu_k) \ln (1 - \nu_k)]. \]

Equations (3) and (4) immediately lead to an expression for the atomic grand potential \( \Omega_a = E_a - TS_a - \mu N_a \). Then, using the relation \( \nu_k = \frac{\text{exp} \left\{ ((\epsilon_k - \mu) / T) + 1 \right\}^{-1} }{1 + \text{exp} \left\{ ((\epsilon_k - \mu) / T) + 1 \right\}^{-1} } \), we obtain for the occupation numbers of atoms:

\[ \nu_k = \frac{\text{exp} \left\{ ((\epsilon_k - \mu) / T) + 1 \right\}^{-1} }{1 + \text{exp} \left\{ ((\epsilon_k - \mu) / T) + 1 \right\}^{-1} } \]

where \( \epsilon_k = \hbar^2 k^2 / 2 M + U_k \), and \( U_k = \sum_{k'} g_{kk'} \nu_{k'} / V \) is the mean field acting on the atom with momentum \( k \). Accordingly, the expression for the grand potential and pressure of the atomic component reads:

\[ \Omega_a = -P_a V = \sum_k [2 T \ln (1 - \nu_k) - U_k \nu_k]. \]

This set of equations is completed by the relation between the density of bosonic molecules and their chemical potential. In the absence of molecular BEC we have:

\[ n_m = \left( \frac{\sqrt{2}}{\Lambda_T} \right)^{3/2} g_{3/2} \text{exp} \left( \frac{\mu_m}{T} \right), \]

where \( g_n(x) = \sum_{j=1}^n x^j / j^6 \), and \( \Lambda_T = (2 \pi \hbar^2 / MT)^{1/2} \) is the thermal de Broglie wavelength for the atoms. For \( n_m \Lambda_T > 7.38 \) the molecular fraction becomes Bose-condensed, and we have \( \mu = 0 \) and \( \mu = -\epsilon_B / 2 \). Similarly,
The energy, entropy, and grand potential of the molecules are given by usual equations for an ideal Bose gas [11].

From Eqs. (4) - (7) we obtain the fraction of unbound atoms \( n_a/n \) and the fraction of atoms bound into molecules, \( 2n_m/n \), as universal functions of two parameters: \( T/\epsilon_B \) and \( nA_T^3 \), where \( n \) is the total density of atomic particles. The dependence of atomic and molecular fractions on \( T/\epsilon_B \) for two values of \( nA_T^3 \) is shown in Fig. 1. The molecular fraction increases and the atomic fraction decreases with decreasing \( T/\epsilon_B \). Occupation numbers of the atoms are always small, whereas quantum degeneracy of molecules is important. The dotted line in Fig. 1b indicates the onset of molecular BEC.

This mixture was realized in the ENS experiment [6], where the occupation numbers for the molecules were up to 0.3 and the molecular fraction was exceeding the atomic one. In the recent studies [23, 21, 22, 20] almost all atoms were converted into molecules by sweeping the magnetic field across the resonance, and at ENS [20] the temperature was within a factor of 2 from molecular BEC. Remarkably, one can modify the molecular fraction and degeneracy parameter \( n_mA_T^3 \) by adiabatically tuning the atom-atom scattering length, as shown in Fig. 2. The decrease of \( a \) increases the binding energy \( \epsilon_B \) and the molecular fraction, and thus causes heating [20]. Close to resonance, \( n_mA_T^3 \) remains almost constant and then decreases due to heating.

The atom-molecule and molecule-molecule interactions are readily included in our approach for \( a \ll A_T \), where the corresponding coupling constants are \( g_{am} = 0.9g \) and \( g_m = 0.3g \) [20]. In this limit the interactions provide an equal shift of the chemical potential and single-particle energy \( \epsilon_B \). For the atoms this shift is \( n_ag/2 + n_mg_{am} \), where the first term is the atom-atom contribution \( U_k \). For the (non-condensed) molecules the shift is \( n_ag_{am} + 2nmg_m \). The entropy of the mixture is given by the same expressions as in the absence of the interactions. As seen in Fig. 1 and Fig. 2, the atom-molecule and molecule-molecule interactions do not significantly modify our results. From Fig. 2 one then concludes that the conditions for achieving molecular BEC are optimal for values of \( a \) as low as possible while still staying at the plateau, as at larger \( a \) the interaction between the molecules can reduce the BEC transition temperature [1].

We now analyze the interaction effect observed at ENS for trapped clouds in the hydrodynamic regime [9]. The experiment was done near the Feshbach resonance located at the magnetic field \( B_0 = 810 \) G, and the data results from two types of measurements of the size of the cloud released from the optical trap. In the first one, the magnetic field and, hence, the scattering length, are kept the same as in the trap. Therefore, the cloud expands with the speed of sound \( c_s = \sqrt{\partial P/\partial \rho} \), where \( \rho = mn \) is the mass density. The speed \( c_s \) and, hence, the size of the expanding cloud are influenced by the presence of molecules and by the interparticle interactions.

In the second type of measurement, the magnetic field is first rapidly ramped down and the scattering length becomes almost zero on a time scale \( t \sim 2\mu s \). This time scale is short compared to the collisional time. Therefore, the spatial distribution of the atoms remains the same as in the initial cloud, although the mean field is no longer present. At the same time, a rapid decrease of \( a \) increases the binding energy of molecules \( \epsilon_B \). However, as the time \( t \lesssim h/\epsilon_B \), they can not adiabatically follow to a deeper bound state and dissociate into atoms which acquire kinetic energy. Thus the system expands symmetrically as an ideal gas of \( N \) atoms, with the initial density profile. The momentum distribution \( f_k \) will be a sum of the initial atomic momentum distribution and one that arises from the dissociated molecules. The latter is found assuming an abrupt change of \( a \) and, hence, projecting

\[
\rho \sim \begin{cases} 
0 & \text{if } B > B^* \\
\rho_n & \text{if } B < B^* 
\end{cases}
\]

FIG. 2: Molecular degeneracy parameter \( n_mA_T^3 \) under adiabatic variation of \( a \) for \(^4\)Li, assuming \( nA_T^3 = 15 \) close to resonance. The dashed curve is obtained including atom-molecule and molecule-molecule interactions. The horizontal dashed line shows the critical value for molecular BEC.

FIG. 3: Calculated (solid line) and measured [9] (squares and crosses) ratio \( \beta \) of the interaction to kinetic energy (see text). The calculated line for \( B > 790G \) is for experimental conditions \( T = 0.9E_F = 3.4\mu K \) and \( n = 3 \times 10^{13} \) cm\(^{-3} \). For \( B < 700G \) we take the averaged experimental conditions \( T = 1.1E_F = 2.4\mu K \) and \( n = 1.3 \times 10^{13} \) cm\(^{-3} \). For \( 700 < B < 800G \), we use the local conditions (see [9]). Inset: Scattering length as a function of magnetic field.
the molecular wave function on a complete set of plane waves. This gives rise to a distribution \( c(q) \) for the relative momenta \( q \). The single-particle momentum distribution for the atoms produced out of molecules results then from convoluting \( c(\mathbf{k} - \mathbf{k}')/2 \) with the molecular distribution function \( \rho_m(\mathbf{k} + \mathbf{k}') \) by integrating over \( \mathbf{k}' \). One can establish a relation between the expansion velocity \( v_0 \) of this non-equilibrium system and the expansion velocity \( v_0 \) of an ideal equilibrium two-component atomic Fermi gas which has the same density and temperature: 

\[
4\pi^2 n \int_0^{\hbar v_0/M} dk k^2 f_k = \int_0^{\hbar v_0/M} dk k^2 \tilde{v}_k, \quad \text{with} \quad \tilde{v}_k \text{being the ideal-gas momentum distribution.}
\]

Using the scaling approach \[24, 25\], one can find that in the spherical case the relative difference between the two squared momenta distributions for the atoms produced out of molecules results as the ratio of the interaction to kinetic energy and called the hydrodynamic Fermi gas in the absence of mean-field interactions. One can establish a relation between the expansion velocity \( c_0 \) and the molecular fraction is already small and the sound velocity \( c_s \) is determined by the molecular cloud. For \( a \ll \Lambda T \) we find \( c_s = 0.4T_0/M + nq_m/2M \), where the second term is provided by the molecule-molecule interaction and is omitted in the high-\( T \) approach. The ratio of this term to the first one is \( \sim 5(na^3)^{1/3} \). For \( B = 700 \text{ G} \) at densities of Ref. \[2\], it is equal to 1 and is expected to grow when approaching the resonance.

Thus, except for a narrow region where \( n|a|^3 \gg 1 \), one can not speak of a universal behavior of the shift \( \beta \) on both sides of the resonance. The situation depends on possibilities of creating an equilibrium atom-molecule mixture. Moreover, at low temperatures the universality can be broken by the molecule-molecule interactions.

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