 Endpoint thermodynamics of an atomic Fermi gas subject to a Feshbach resonance

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The entropy and kinetic, potential, and interaction energies of an atomic Fermi gas in a trap are studied under the assumption of thermal equilibrium for finite temperature. A Feshbach resonance can cause the fermions to pair into diatomic molecules. The entropy and energies of mixtures of such molecules with unpaired atoms are calculated, in relation to recent experiments on molecular Bose-Einstein condensates produced in this manner. It is shown that, starting with a Fermi gas of temperature $T = 0.17 T_F$, where $T_F$ is the non-interacting Fermi temperature, an extremely cold degenerate Fermi gas of temperature $T \lesssim 0.01 T_F$ may be produced without further evaporative cooling. This requires adiabatic passage of the resonance, subsequent sudden removal of unpaired atoms, and adiabatic return. We also calculate the ratio of the interaction energy to the kinetic energy, a straightforward experimental signal which may be used to determine the temperature of the atoms and indicate condensation of the molecules.

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I. INTRODUCTION

The formation of cold diatomic molecules from an atomic Fermi gas offers one the opportunity to study the Bose-Einstein condensate to Bardeen-Cooper Schrieffer (BEC to BCS) crossover in an atomic system [1-4]. Cold atomic gases present several advantages in investigations of this long-standing problem: they are impurity-free; their temperature, density, and interaction strength can be tuned over wide ranges; and they are easily manipulated with lasers. The key to obtaining superfluid states such as BEC and BCS is to cool the gas to a sufficiently low temperature [5].

In recent experiments, Feshbach resonances have been used to transform a cold or degenerate Fermi gas into a molecular BEC [6, 7, 8, 9, 10, 11]. A Feshbach resonance is a resonance between an unbound atomic state and a bound molecular state brought about by the Zee-man effect, in practice by changing a uniform magnetic field over the region of the gas [12]. The molecular pairing mechanism is a few-body effect brought about by the Feshbach resonance. The BCS pairing mechanism is a many-body effect due to an instability at the Fermi surface. This interplay between few and many body physics is an outstanding problem. Various theories have been proposed to model the crossover region and molecule formation [13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. However, in order to study the crossover thoroughly it is desirable to have clearly defined and demonstrated endpoints.

In the following, basic thermodynamic quantities related to the endpoints of this problem are calculated: in particular, the kinetic energy, potential energy, interaction energy, and the entropy. Two cases are considered: (a) a degenerate atomic Fermi gas of two spin states interacting via a weakly attractive contact potential; and, (b) an atom-molecule mixture in which the atoms and molecules interact both with themselves and with each other via a repulsive contact potential, as was the case in the experiment of Ref. [6]. The atomic interaction parameter is given by $k_F^0|a|$, where $k_F^0$ is the non-interacting Fermi momentum and $a$ is the $s$-wave scattering length. The $s$-wave scattering length is a function of the magnetic field in the region of the resonance and typically changes over many orders of magnitude as well as in sign. Case (a) treats the parameter regime $a < 0$ and $k_F^0|a| \ll 1$, for which a weakly interacting BCS-type transition is possible. Case (b) treats the regime $a > 0$ and $k_F^0|a| \ll 1$, in which case the molecules may Bose condense. In case (b) both a Boltzmann-like molecular gas of $T/T_{BEC} \gg 1$ and a degenerate molecular gas of $T/T_{BEC} \ll 1$ are considered. Two applications which demonstrate the usefulness of these calculations in relation to present experiments are illustrated.

Firstly, we present a straightforward signal for the onset of condensation in the molecules. The ratio of the interaction energy to the kinetic energy is an established observable [23]. The power law in this ratio changes as the molecules are condensed. Moreover, this quantity can be used to determine the temperature, which, particularly in case (b) for $T \ll T_{BEC}$, would be difficult to determine for the atoms from momentum distributions alone, since they are pushed to the edges of the molecular cloud by the molecular mean field, as we shall show. This ratio is thought to be a universal constant in the unitarity limit, i.e., when $k_F^0|a| \gtrsim 1$, where it is called $\beta$ in the literature [24, 25].

Secondly, we propose a new way to obtain a sufficiently low temperature for a weakly interacting BCS transition. A recent proposal [24] showed that adiabatic transition of the resonance from degenerate molecules to atoms leads to cooling. This follows from the fact that the entropy of an ideal fermionic gas $S_F \propto T$ while the entropy of an ideal bosonic gas $S_m \propto T^3$ [26]. Holding the entropy constant results in a decreased temperature for sufficiently small $T$. The addition of weak interactions does not change this fact [21]. In the experiment of Ref. [6], it was found that, after tuning the atoms over the resonance so that they formed molecules, about 15% of the atoms remained unpaired [23] In such an atom-molecule mixture,
at low temperature, the majority of the entropy resides in the atoms. Therefore, suddenly removing the atoms is the same as removing entropy. The technique of removing atoms while leaving the molecules in place has been experimentally demonstrated \[29\]. Adiabatically dissociating the molecules then leads to an extremely cold fermionic gas of temperatures \( T \lesssim 0.01T_F \), where \( T_F \) is the Fermi temperature. We term this cooling method entropic cooling. Given the experimental limitations of evaporative cooling, which for a BEC is \( T \approx 0.25T_{\text{BEC}} \) and for a Fermi gas is \( T \approx 0.05T_F \) (see, for example, Refs. \[31\] and \[32\], respectively), entropic cooling provides an attractive alternative.

We note that a recent experiment has successfully traversed the crossover from a molecular BEC to an atomic Fermi gas in a sufficiently adiabatic manner to achieve entropic cooling \[32\].

The presentation may be outlined as follows. In Sec. \[II\] the model is presented. In Sec. \[III\] the thermodynamic quantities are calculated for a degenerate Fermi gas, in some detail. In Sec. \[IV\] the same quantities are presented for the atom–molecule mixture at temperatures both above and below \( T_{\text{BEC}} \). In Sec. \[V\] the two experimental applications are considered: a signal for the onset of molecular BEC; and the use of entropic cooling to achieve temperatures sufficiently low for a BCS transition. Finally, in Sec. \[VI\] we conclude.

**II. THE MODEL**

Our model consists of the following assumptions. Firstly, it is supposed that for negative scattering length \( T > T_{\text{BCS}} \) and \( k_B^2|a| < 1 \). This assures that the system is far from resonance and that there is no superfluid phase. Secondly, for positive scattering length the dilute limit \( \sqrt{n_{am}a_{am}} \ll 1 \) is assumed for the molecules, where \( n_{am} \) is the average molecular density and the molecule–molecule and atom–molecule scattering lengths \( a_{mm}, a_{am} \propto a \), with \( a \) the \( s \)-wave atom–atom scattering length. The proportionality constants are taken to be 0.6 and 1.2, respectively, in accord with Petrov et al. \[10\], where it is calculated explicitly in certain limits from the four body problem. Thirdly, it is assumed that the atoms and molecules can be treated as distinct entities: the former are fermions and the latter are bosons, whose thermodynamic properties can be calculated separately. Fourthly, it is assumed that the system is in thermal equilibrium. However, it is not necessary to require chemical equilibrium. The former requires a sufficiently high rate of elastic two body collisions \((A + A \leftrightarrow A + A, M + A \leftrightarrow M + A)\); as the latter is brought about by three-body collisions \((A + A + A \leftrightarrow M + A)\), it may be substantially slower. This indeed appears to be case in certain experiments \[8\] \[15\] \[28\] \[31\].

Fifthly, it is assumed that the atom–molecule coupling for binary interactions is given by the \( s \)-wave limit \( g = 2\pi\hbar^2a/m_r \), where \( m_r = m_a/2 \) is the reduced mass. The atom–molecule and molecule–molecule coupling is then \( g_{am} = 0.9g \) and \( g_{mm} = 0.3g \) according to Ref. \[10\]. Sixthly, it is assumed that both atoms and molecules are subject to the same isotropic harmonic trapping frequency \( \omega \). Thus their densities shall also be isotropic, as well as all other thermodynamic quantities \[34\]. Seventhly, it is assumed that for negative scattering length there are an equal number of spin up and spin down atoms. It is now possible to change the scattering length from negative to positive, selectively remove excess atoms of both spin states, and then change the scattering length back to negative, thereby resulting in the precise balance assumed here \[29\]. This results in a pleasant symmetry in the thermodynamic expressions, as well as avoiding Fulde-Ferrell-Larkin-Ovchinnikov phases when a BCS transition is sought (see Ref. \[33\] and references therein).

Eightly, the local density and semi-classical approximations, which are valid for \( k_B T > 1/\rho(E_F) \), are assumed to hold, where \( \rho(E_F) \) is the density of states at the Fermi surface.

The critical temperature for condensation of an ideal gas shall be denoted as

\[
k_B T_{\text{BEC}}^0 = \hbar \omega \left[ \frac{N_m}{\zeta(3)} \right]^{1/3},
\]

where \( N_m \) is the number of molecules and \( \zeta \) is the Riemann Zeta function. The shift in this temperature caused by interactions may be calculated to be \[36\]

\[
\frac{\delta T}{T_{\text{BEC}}^0} = -1.3 \frac{a_{am}}{\hbar \omega} N_m^{1/6}
\]

in a harmonic trap for the assumed regime of \( \sqrt{n_{am}a_{mm}} \ll 1 \), where

\[
\hbar = \sqrt{\frac{\hbar}{m_m \omega}}
\]

is the harmonic oscillator length. Therefore a ninth assumption is that this shift is small, so that it may be neglected in our calculations \[37\]. This is consistent with the second assumption above. Typical shifts in experiments are less than 10%. Similarly, the Fermi temperature will be denoted by its ideal value of

\[
k_B T_F^0 = \hbar \omega (3N_a)^{1/3},
\]

where \( N_a \) is the number of atoms.

Lastly, for \( T < T_{\text{BCS}} \), the Thomas-Fermi profile shall be assumed for the bosonic molecules:

\[
n_m^{TF}(r) = \frac{\mu_m}{g_{mm}} \left( 1 - \frac{r^2}{R_m^2} \right), \quad r \leq R_m,
\]

\[
\mu_m = \frac{1}{2} m_m \omega^2 R_m^2,
\]

where the subscript \( m \) refers to molecules, \( m_m = 2m_a \) and \( \mu_m \) is the molecular chemical potential. Note that \( n_m^{TF}(r) = 0 \) for \( r \geq R_m \).
III. NEGATIVE SCATTERING LENGTH: ATOMS ONLY

We first consider the case for which the scattering length is negative, so that there are no molecules. We calculate the entropy and the energy. The energy is divided into kinetic, potential, and interaction parts. For an isotropic harmonically trapped cold atomic gas, the potential energy

\[ V(r) = \frac{1}{2} m_\alpha \omega^2 r^2 \]  

represents the trap energy and

\[ U_{\text{mf}}(r) = \frac{1}{2} gn_\alpha(r) \]  

is the interaction or mean field energy, where \( n_\alpha(r) \) is the total mean field particle density, i.e., including both spin states, and \( g \) is the interaction strength. The expressions are derived in some detail in this, the simplest case, in order to serve the reader as a model for similar calculations which are only sketched in the following sections.

A. Energy

The expressions for the energy in the local density approximation are given by integrals over phase space of the form

\[ E_{\text{kin}} = 2 \int \frac{d^3r d^3p}{(2\pi\hbar)^3} \frac{p^2}{2m_\alpha} \nu(r,p), \]  

\[ E_{\text{pot}} = 2 \int \frac{d^3r d^3p}{(2\pi\hbar)^3} \frac{1}{2} m_\alpha \omega^2 r^2 \nu(r,p), \]  

\[ E_{\text{int}} = \int d^3r g \left[ \frac{1}{2} n_\alpha(r) \right]^2, \]  

where

\[ \nu(r,p) = \{ \exp[\beta(E(r,p) - \mu)] + 1 \}^{-1} \]  

is the mean occupation number,

\[ \beta \equiv \frac{1}{k_B T}, \]  

and

\[ E(r,p) \equiv \frac{p^2}{2m_\alpha} + V(r) + U_{\text{mf}}(r) \]  

is the total energy in phase space. The factor of 2 in front of the integrals in Eqs. (9) and (11) is due to the number of spin states.

One may obtain self-consistent expansions to first order in \( k_F^0|a| \) and second order in \( T/T_F^0 \), where

\[ k_F^0 \equiv \sqrt{2m_\alpha k_B T_F^0}/\hbar. \]  

is the Fermi momentum defined with respect to an ideal gas. The key is to set \( n_\alpha(r) = n_\alpha^0(r) \) in \( U_{\text{mf}}(r) \) and Eq. (11), where

\[ n_\alpha^0(r) = \frac{1}{4} \left( \frac{2m_\alpha}{\pi\hbar^2} \right)^{3/2} g_{3/2}(-e^u), \]  

\[ u \equiv \beta \left( \mu_\alpha - \frac{1}{2} m_\alpha \omega^2 r^2 \right), \]  

is the non-interacting density profile, which may be obtained by integrating Eq. (12) over momentum space. The function \( g_{3/2}(x) \) in Eq. (16) is the Bose function [27]. The details of the calculation are presented in App. A.

One finds

\[ E_{\text{kin}} = N k_B T_F^0 \left[ \frac{3}{8} + \frac{256}{315\pi^2} k_F^0 |a| \right] \]  

\[ + \left( \frac{\pi^2}{4} - \frac{184}{35} k_F^0 |a| \right) \left( \frac{T}{T_F^0} \right)^2, \]  

\[ E_{\text{pot}} = N k_B T_F^0 \left[ \frac{3}{8} - \frac{256}{315\pi^2} k_F^0 |a| \right] \]  

\[ + \left( \frac{\pi^2}{4} - \frac{136}{35} k_F^0 |a| \right) \left( \frac{T}{T_F^0} \right)^2, \]  

\[ E_{\text{int}} = -N k_B T_F^0 k_F^0 |a| \left[ \frac{1024}{945\pi^2} - \frac{32}{35} \left( \frac{T}{T_F^0} \right)^2 \right]. \]  

These expressions may be shown to be self-consistent in two ways. Firstly, one observes that the virial theorem

\[ 2E_{\text{kin}} - 2E_{\text{pot}} + 3E_{\text{int}} = 0 \]  

holds up to first order in \( k_F^0 |a| \) and to second order in \( T/T_F^0 \). Secondly, note that the total energy at zero temperature for an ideal gas is \( E_{T=0} = E_{\text{kin}} + E_{\text{pot}} = \frac{3}{4} N E_F^{\text{total}} \), as may also be calculated directly from the density of states for an ideal Fermi gas in a harmonic trap. The expansions given by Eqs. (18), (19), and (20) are accurate to 1%, 5%, and 24% for \( k_F^0 |a| = 0.1 \) and \( T/T_F^0 = 0.1 \). For higher temperature or stronger interaction strength, the accuracy becomes quite poor, for example 72%, 35%, and 233% for \( k_F^0 |a| = 0.5 \) and \( T/T_F^0 = 0.5 \). In this case it is preferable to evaluate the energy integrals self-consistently in the mean field by recursive use of Eqs. (9) - (11) with the density profile

\[ n_\alpha(r) = 2 \int \frac{d^3p}{(2\pi\hbar)^3} \nu(r,p), \]  

while holding the total number of atoms, given by the integration of Eq. (22) over volume, constant. This gives the exact result, which we have used to evaluate the accuracy of the expansions.

In Fig. 4 is shown the ratio of the interaction energy to the kinetic energy in the degenerate regime. This quantity is a straightforward experimental observable [25], which can be used to determine the temperature of the system. The figure shows the self-consistent
The local density approximation in an isotropic system, the probability to be in a given state \[38\]. For fermions in integrated over momentum to obtain

\[ \text{where the factor of 2 is due to the two atomic spin states} \]

\[ \text{transition are on the order of one-half} \[26\]. \]

almost strongly interacting regime. In a recent work, it
ularly important for the upper curve, which treats the

tal observable \[23\] that may be used to measure the degen-


degenerate Fermi gas. This ratio is an established experime n-


tic observable as a function of \[25\]. The method for doing so is outlined in App. \[A\]. One obtains

\[
\frac{S}{k_B} = 2 \left( \frac{k_B T}{\hbar \omega} \right)^3 \left[ \beta \mu_a \left( -e^{-\beta \mu_a} \right) - 4 g_4 \left( -e^{-\beta \mu_a} \right) \right].
\] (26)

In the degenerate limit, \( \beta \mu_a \gg 1 \), the Bose functions may be expanded to obtain (see Eq. \[A11\] in App. \[A\])

\[
S = k_B \pi^2 N \left( \frac{T}{T_F} \right)^3 (\beta \mu_a)^2
\] (27)
to lowest order in \( T/T_F \). As in Sec. \[III A\] corrective terms due to the interactions may be obtained in powers of \( k_F |a| \). The method for doing so is outlined in App. \[A\].

IV. POSITIVE SCATTERING LENGTH:
MOLECULE-ATOM MIX

We next consider the case of positive scattering length, for which there is a mixture of atoms and molecules, as in the experiment of Ref. \[6\]. In the following, it shall be assumed that the molecular mean field acts on the atoms, but that the effect of the atomic mean field on the molecules is negligible. This is justified for small fractions of atoms, which is the case experimentally. The effect of the atomic and molecular mean fields on themselves, respectively, shall be calculated to first order in the interactions, as was done in the previous section for negative scattering length.

A. Above the Molecular Condensation Temperature

1. Molecules

The entropy and kinetic, potential, and interaction energies of the molecules may be calculated by similar methods to those presented explicitly in Sec. \[III\]. The local density approximation for the energy in phase space is

\[
E(r,p) = \frac{p^2}{2m_m} + \frac{1}{2} m_m \omega^2 r^2 + g_{mm} n_m(r)
\] (29)

One may take the mean field density profile to be the non-interacting one, i.e., \( n_m(r) = \frac{1}{2} n_a^{(0)}(r) \) (as in Eq. \[10\]).
with all $a$ subscripts changed to $m$, where the factor of one half is to account for the number of spin states. Then the resulting energies are:

$$E_{\text{kin}} = \frac{3}{2} N_m k_B T \left[ 1 - \frac{\zeta(3)}{16} \left( \frac{T_{\text{BEC}}^0}{T} \right)^3 \right],$$

$$E_{\text{pot}} = \frac{3}{2} N_m k_B T \left[ 1 + \frac{3\zeta(3)}{10\sqrt{2}} \left( \frac{T_{\text{BEC}}^0}{T} \right)^{5/2} \right],$$

$$E_{\text{int}} = N_m k_B T \frac{3\zeta(3)}{10\sqrt{2}} \left( \frac{T_{\text{BEC}}^0}{T} \right)^{5/2},$$

to cubic order in $T_{\text{BEC}}^0/T$ and leading order in the mean field in Eq. (28), where

$$\gamma \equiv \left[ \frac{N_m}{24\pi^3 \zeta(3)} \frac{1}{k_F^3} \right]^{1/6} \frac{k_B T_{\text{BEC}}^0}{\pi E_B},$$

and

$$E_B = \frac{\hbar^2}{m_a a^2}$$

is the approximate binding energy of the molecule. Appendix C gives the perturbative expression for the molecular fugacity, which is useful in obtaining the energies, in that one must eliminate the chemical potential in order to obtain energies depending on temperature and atomic/molecular number alone.

Note that the large temperature non-interacting limit is given by $E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}} = 3N_m k_B T$. This agrees with a simple calculation based on the density of states: $E_{\text{tot}} = \int dE E^3 e^{\beta E} (\rho_{\text{BEC}} - \rho_b) / (\hbar \omega) = 3N_m k_B T + O(T^0)$. The expansions given by Eqs. (30), (31), and (32) are accurate to 0.66%, 2.4%, and 6.4% for $k_F^0 |a| = 0.5$ and $T/T_{\text{BEC}}^0 = 1$. For higher temperature or weaker interaction strength, they are accurate to better than 1%.

The physically measurable quantity

$$\frac{E_{\text{int}}}{E_{\text{kin}}} = \frac{\zeta(3)}{5\sqrt{2}} \left( \frac{T_{\text{BEC}}^0}{T} \right)^{5/2} \gamma,$$

(C5) to leading order, in contrast to the power law for Bose condensed molecules, as shall be discussed in Sec. IV A 3.

The entropy is calculable by similar techniques as were used to obtain the energies, either from the combinatoric expression similar to the calculation of Sec. III B or from the grand potential (see, for example, Ref. 26).

2. Atoms

The energy of the atoms in phase space is

$$E(r,p) = \frac{p^2}{2m_a} + \frac{1}{2} m_a \omega^2 r^2 + g \frac{n_a(r)}{2} + g_{am} n_m(r). \quad (36)$$

Note the inclusion of the molecular mean field. The atom-atom and atom-molecule interaction energies are

$$E_{\text{int}}^{\text{aa}} = g \int d^3 r \left( \frac{n_a(r)}{2} \right)^2,$$

$$E_{\text{int}}^{\text{am}} = g_{am} \int d^3 r n_a(r) n_m(r), \quad (37)$$

respectively, while the kinetic and potential energies are calculated in analogy with Eqs. (38) and (39). One finds

$$E_{\text{kin}} = N_a k_B T \left[ \frac{3}{2} + \frac{3 N_a \zeta(3)}{64 N_m} \right] \left( \frac{T_{\text{BEC}}^0}{T} \right)^3 \] \right],$$

$$E_{\text{pot}} = N_a k_B T \left[ \frac{3}{2} + \frac{N_a \zeta(3)}{64 N_m} \right] \left( \frac{T_{\text{BEC}}^0}{T} \right)^3 \] \right],\quad (39)$$

$$+ \zeta(3) \left( \frac{N_a}{N_m} \right) \left( \frac{T_{\text{BEC}}^0}{T} \right)^{5/2},$$

$$E_{\text{int}}^{\text{aa}} = N_a k_B T \frac{N_a \zeta(3)}{8} \gamma \left( \frac{T_{\text{BEC}}^0}{T} \right)^{5/2},$$

$$E_{\text{int}}^{\text{am}} = N_a k_B T \frac{2 \sqrt{3} \zeta(3)}{5} \gamma \left( \frac{T_{\text{BEC}}^0}{T} \right)^{5/2}, \quad (40)$$

where the expansions have been made to cubic order in the small parameter $T_{\text{BEC}}^0/T$ and to lowest order in the atomic and molecular mean fields in Eq. (39). Appendix D gives the perturbative expressions for the atomic and molecular fugacities, which are useful in obtaining the energies. Note that, as in Sec. IV A 1.
the large temperature non-interacting limit is given by $E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}} = 3\hbar c k_B T$. The expansions given by Eqs. (8), (10), and (11) are accurate to 0.006%, 1%, 4%, and 4% for $k_B T [\alpha] = 0.5$ and $T/T_B^{\text{BEC}} = 2$. For higher temperature or weaker interaction strength, the accuracy rapidly improves. In the most extreme limits, e.g., $T/T_B^{\text{BEC}} = 1$, the accuracies are on the order of 10% to 50%.

The correct virial theorem must be modified from that of Eq. (21):

$$2E_{\text{kin}} - 2E_{\text{pot}} + 3E_{\text{int}} = 0 .$$

(43)

Note that, according to the above expressions, the condition for chemical equilibrium, $2\mu_a = -E_B + \mu_m$, which we have not assumed here [17], would give

$$N_m/N_a = 2\sqrt{\frac{\zeta(3)}{2}} \left(\frac{T_B^{\text{BEC}}}{T}\right)^{3/2} e^{\beta E_B/2}$$

(44)

for $T_B^{\text{BEC}}/T \ll 1$.

The entropy of the atoms may be calculated by integrating numerically over the general expression for the entropy density given by Eq. (27) with

$$u = \beta [\mu_a - \frac{1}{2} m_a \omega^2 r^2 - \frac{1}{2} g n_a(r) - g_m n_m(r)].$$

(45)

An expansion may also be developed in order to determine a perturbative expression in the Boltzmann limit in the same fashion as was done for the energies.

B. Below the Molecular Condensation Temperature

1. Molecules

The chemical potential of the molecules may be calculated from the Thomas-Fermi profile $n^{TF}_m(r)$ to be

$$\mu_m = \left(3 \cdot 5 \frac{\sqrt{2}}{2^{24} \pi}\right)^{2/5} (g_{mm} N_m)^{2/5} (m_\omega^2)^{3/5} .$$

(46)

The energy in phase space is given by the energy of Boguliubov quasiparticle excitations (see [26] and references therein):

$$E(r,p) \equiv \left\{ \begin{array}{ll} \frac{p^2}{2m_m} + 2 g_{mm} n_m^{TF}(r) & |r| \leq R_m \\ \frac{p^2}{2m_m} + m_\omega^2 \frac{r^2}{2} - \mu_m & |r| > R_m . \end{array} \right.$$  

(47)

The energies may then be solved for as

$$E = \frac{8 N_m}{\pi \zeta(3)} \left(\frac{T}{T_B^{\text{BEC}}}\right)^3 k_B T f(\beta \mu_m) ,$$

(48)

where the integrals for the kinetic, potential, and interaction energies are defined respectively by

$$\begin{align*}
\int \text{kin}(\beta \mu_m) & \equiv (\beta \mu_m)^{3/2} \left\{ \int_0^1 dx x^2 \int_0^\infty dy \frac{y^{3/2}}{\exp[y/g + 2(1-x^2)] - 1} + \frac{3\sqrt{\pi}}{4} \int_1^\infty dx x^{2k/2} g_5/2[e^{\beta \mu_m(1-x^2)}]\right\} , \quad (49) \\
\int \text{pot}(\beta \mu_m) & \equiv (\beta \mu_m)^{5/2} \left\{ \int_0^1 dx x^4 \int_0^\infty dy \frac{y^{1/2}}{\exp[y/g + 2(1-x^2)] - 1} + \frac{\sqrt{\pi}}{2} \int_1^\infty dx x^4 g_3/2[e^{\beta \mu_m(1-x^2)}]\right\} , \quad (50) \\
\int \text{int}(\beta \mu_m) & \equiv (\beta \mu_m)^{5/2} \left\{ \int_0^1 dx x^2 (1-x^2) \int_0^\infty \frac{dy y^{1/2}}{\exp[y/g + 2(1-x^2)] - 1}\right\} . \quad (51)
\end{align*}$$

Note that the virial theorem, Eq. (21), holds.

The entropy has been calculated elsewhere in detail from the exact density of states [26]:

$$\rho(\epsilon) = [\mu_m / (\pi \hbar^3 \omega^3)] \left\{ 2 \sqrt{2} \pi \frac{\tan^{-1} \left[ \sqrt{2} \pi / (1 + z) \right]}{z^{3/2} - \sqrt{2} \pi [2 + \tan^{-1} (1 - z) / \sqrt{2} z]} + (1 + z)^2 \theta_0 - \sin (4 \theta_0/4) \right\} ,$$

(52)

where $z \equiv \epsilon / \mu_m$ is the rescaled energy and $\theta_0 \equiv \cos^{-1} (1 / \sqrt{1 + z})$. The result is

$$S = \frac{\nu_m}{\zeta(3)} \left(\frac{T}{T_B^{\text{BEC}}}\right)^3 G(\beta \mu_m) ,$$

(53)

where

$$G(\beta \mu_m) \equiv (\beta \mu_m)^3 \int_0^\infty dz f(z) \left[ \frac{\beta \mu_m z}{e^{\beta \mu_m z} - 1} - \ln (1 - e^{-\beta \mu_m z}) \right] ,$$

(54)

and

$$f(z) \equiv \frac{(\hbar \omega)^3}{\mu_m^2} \rho(\epsilon) \quad (55)$$

so as to make the units explicit. Note that $G(1) = 8.32$. 
the integrands of the energies. Therefore the energies are left determined up to an integration which may be performed numerically for a given parameter set, as in Eqs. (57) - (59).

The entropy of the atoms may again be calculated by integrating numerically over the general expression for the entropy density given by Eq. (25) with

\[ u \equiv \beta \left[ \mu_a - \frac{1}{2} m_a \omega^2 r^2 - \frac{1}{2} g n_a(r) - g_{am} n_m(r) \right] \tag{59} \]

V. APPLICATION TO EXPERIMENTS

The entropies and energies calculated in Secs. III and IV are useful in understanding experiments. In the following, two examples are given. In Figs. 3 and Table I the parameters of the recent JILA molecular BEC experiment [2] are used throughout.

A. Evidence of molecular condensation and atom-molecule temperature

The dependence of the ratio of the interaction energy to the kinetic energy on temperature is a useful experimental observable. It is obtained via time-of-flight measurements with and without interactions; the interactions
can be rapidly switched on or off via a Feshbach resonance \( 2 \). This ratio allows one to determine the degeneracy in the case of negative scattering length (see Fig. 4). In the case of positive scattering length, when one has an atom-molecule mixture, it can again be used to calculate the temperature of the atoms. This is particularly important as their temperature dependence cannot be determined in a simple way from their momentum distribution, due to the fact that the atoms occupy a spherical shell outside the region of the molecular mean field (see Fig. 2). In Fig. 3 is shown this ratio, calculated for \( T \) both above and below \( T^0_{\text{BEC}} \), from the integral equations of Secs. IV A 2 and IV B 2. In the case of molecules, the dependence of the ratio of interaction to kinetic energy on degeneracy signals the onset of condensation. Above \( T^0_{\text{BEC}} \), \( E_{\text{int}}/E_{\text{kin}} \propto (T/T^0_{\text{BEC}})^{-5/2} \), while below \( E_{\text{int}}/E_{\text{kin}} \propto (T/T^0_{\text{BEC}})^{-1} \). The result is illustrated in Fig. 4 as calculated from the energy equations of Secs. IV A and IV B. Both figures use the parameters of the JILA experiment \( 6 \). Note that the fact that the left hand and right hand curves in Figs. 3 and 4 do not meet is due to our use of the Thomas-Fermi approximation for the mean field of the molecular condensate. The use of this approximation changes the form of the left hand curves as \( T \to T^0_{\text{BEC}} \) from below; the right hand curves are exact.

\[ T_{\text{BCS}}/T^0_F = 0.277 \exp \left( -\frac{\pi}{2k_F^0|a|} \right). \]  

(60)

For \( k_F^0|a| = 1/2 \), the temperature necessary to achieve BCS is \( T_{\text{BCS}} = 0.012 T^0_F \). Present evaporative cooling methods have been unable to achieve temperatures below about \( T = 0.05 T_F \). Recently, it was suggested that adiabatic transition across a Feshbach resonance could be used to transform a molecular BEC into a very cold Fermi gas, of sufficiently temperatures to achieve BCS \( 2 \). This is due to the fact that the entropy of fermions is proportional to \( T \) while that of bosons is proportional to \( T^3 \). This scheme requires evaporative cooling of the molecular BEC. The typical maximal degeneracy achievable in an atomic BEC experiment is \( T/T^0_{\text{BEC}} \approx 1/4 \).

Consideration of an atom-molecule mixture presents another alternative. Rather than trying to lower the temperature of the system by evaporative cooling, one may instead attempt to decrease the entropy. Since entropy is held constant across the Feshbach resonance, this amounts to decreasing the final temperature of the Fermi gas. In Fig. 3 is shown the total entropy of an atom-molecule mixture for the JILA parameters \( 6 \) according to the expressions derived in the preceding sections. As illustrated in the figure, the atoms contribute the majority of the total entropy when the Bose gas is degenerate. It has been demonstrated experimentally that the atoms can be selectively removed from an atom–molecule mixture \( 2 \). We therefore propose the following cooling scheme:

1. A pseudo-spin-1/2 Fermi gas is evaporatively cooled to degenerate temperatures for a small negative scattering length \( (k_F^0|a| \ll 1) \).

2. A uniform external magnetic field is changed across a Feshbach resonance so as to cause the atoms to be transformed into molecules, slow enough to ensure thermal equilibrium. The scattering length is now small and positive \( (k_F^0|a| \ll 1) \), or, equivalently, \( n^{1/3} a \ll 1 \).

3. A small number of atoms remain unpaired \( 4 \). These atoms are suddenly removed from the system, thereby reducing the entropy.

4. The system is swept adiabatically back across the Feshbach resonance to a small, negative scattering length. All molecules dissociate into atoms. The resulting Fermi gas has a reduced temperature.

5. The sequence is repeated until temperatures needed to obtain a BCS transition are achieved.

In Table II is presented a realization of this scheme, utilizing parameters similar to those of Ref. \( 6 \), where typically 85% of the atoms are converted into molecules. After three sweeps through the resonance, the final temperature of \( T = 0.0010 T^0_F \) is so low as to be out of the range of the semi-classical approximation. Detailed requirements on the adiabatic transition times and loss rates in the system have been presented elsewhere \( 2 \).
TABLE I: An application of entropic cooling. The left two columns depict the degeneracy and total number of fermionic atoms for negative scattering length. After adiabatic tuning via a Feshbach resonance to positive scattering length (right facing arrow), 84% of the atoms are transformed into bosonic molecules. In the two right hand columns are shown the resulting entropy and degeneracy. The remaining atoms are then suddenly removed, thereby decreasing the entropy of the system, as shown in the third column of the next row. After tuning back (left hand arrow), the temperature is reduced. After several repetitions of this process, the degeneracy is high enough to achieve a weakly interacting BCS transition.

| $T/T_F$ | $N_a$ | Switching | Entropy ($k_B$) | $T/T_{REC}$ |
|---------|-------|------------|-----------------|-------------|
| 0.100   | 200,000 | →          | 217,000         | 0.640       |
| 0.0504  | 167,000 | ←          | 91,300          | 0.640       |
| 0.0504  | 167,000 | ←          | 91,300          | 0.380       |
| 0.0147  | 139,000 | ←          | 22,300          | 0.380       |
| 0.0147  | 139,000 | →          | 22,300          | 0.120       |
| 0.00103 | 116,000 | ←          | 1,301           | 0.120       |

We note that, for the purposes of the table, it was assumed that $g_{am} = 0.9g$ and $g_{nm} = 0.3g$, where $g_{am}$ and $g_{nm}$ are the couplings for atom–molecule and molecule–molecule interactions. This was necessary in order to properly treat the effects of the atomic and molecular mean fields.

VI. CONCLUSIONS

The entropy and kinetic, interaction, and potential energy of fermionic atoms and bosonic molecules were calculated for temperatures both above and below $T_F^0$ and $T_{REC}^0$. The effect of the atomic and molecular mean fields were taken into account both perturbatively in analytic expansions and self-consistently, as illustrated in the figures. Below the condensation temperature, the molecular mean field was assumed to be in the Thomas-Fermi limit and the thermal cloud was neglected. The general method of performing these thermodynamic calculations was outlined.

Two applications of the calculations were then proposed. Firstly, it was shown that the ratio of the kinetic to interaction energy is sufficient to determine the degeneracy of the atoms. The same ratio, for the molecules, may be used to indicate the onset of Bose condensation, as the power law dependence on the degeneracy changes from an exponent of $-5/2$ to $-1$. Secondly, it was suggested that an adaption of entropic cooling could be used to cool a Fermi gas to sufficiently high degeneracy so as to achieve a weakly interacting BCS transition, without the need for evaporative cooling of either the fermionic atoms or the bosonic molecules. This scheme involves tuning adiabatically back and forth through a Feshbach resonance: on the positive scattering length side, the sudden removal of remaining unpaired atoms corresponds to a large reduction in entropy, which, after return to the negative scattering length, results in a decreased temperature. For example, for a conversion efficiency of atoms to molecules of 85%, as in Ref. [6], and starting with a Fermi gas of degeneracy $T/T_F^0 = 0.1$, after three sweeps the degeneracy is increased by two orders of magnitude to $T/T_F^0 = 0.001$ with a loss of less than half of the atoms.

We note that entropic cooling was used successfully for the first time in a recent experiment.

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APPENDIX A: CORRECTION TO THE KINETIC, POTENTIAL, AND INTERACTION ENERGIES FOR A WEAKLY INTERACTING FERMI GAS

Beginning with the general expressions for the energies given by Eqs. 9 - 11, one may integrate over momentum to obtain

$$E_{\text{kin}} = A_{\text{kin}} \int_0^\infty dy y^{1/2} g_{5/2} (-e^u) , \quad (A1)$$

$$E_{\text{pot}} = A_{\text{pot}} \int_0^\infty dy y^{3/2} g_{3/2} (-e^y) , \quad (A2)$$

$$E_{\text{int}} = A_{\text{int}} \int_0^\infty dy y^{1/2} \left[ \frac{1}{2} g_{3/2} (-e^y) \right]^2 , \quad (A3)$$

where

$$u \equiv \beta \left[ \mu_a - y - \frac{1}{2} g_{n_a} (r) \right] , \quad (A4)$$

$$y \equiv \frac{1}{2} \beta m_a \omega^2 r^2 , \quad (A5)$$

and

$$A_{\text{kin}} = -\frac{18N}{\sqrt{\pi}} \left( \frac{T}{T_F^0} \right)^3 k_B T , \quad (A6)$$

$$A_{\text{pot}} = -\frac{12N}{\sqrt{\pi}} \left( \frac{T}{T_F^0} \right)^3 k_B T , \quad (A7)$$

$$A_{\text{int}} = -\frac{6N}{\pi} \left( \frac{T}{T_F^0} \right)^{7/2} k_B T k_F^0 |a| . \quad (A8)$$

To resolve the integrals to first order in the interactions, it is sufficient to assume a mean field given by
the non-interacting density profile of Eq. (16). Then, one may expand the Bose functions in the integrands of Eqs. (A9) - (A11) as
\[
g_n \left( -\exp \left[ \beta \mu_a - y - \alpha g_{3/2} \left( -e^{\beta \mu_a - y} \right) \right] \right) \\
\sim g_n \left( -\exp (\beta \mu_a - y) \right) \\
\quad - \alpha g_{3/2} \left( -\exp (\beta \mu_a - y) \right) g_{n-1} \left( -\exp (\beta \mu_a - y) \right), \quad (A9)
\]
where
\[
\alpha \equiv |a| \sqrt{\frac{2m}{\hbar^2 \pi}}. \quad (A10)
\]
is the small expansion parameter. The maximum value of the Bose function in the non-interacting density occurs for \( y = 0 \) for positive \( \beta \mu_a \). In the limit \( \beta \mu_a \gg 1 \), the Bose function may be expanded as
\[
g_n \left( -e^y \right) = -e^{\nu n} \left[ \frac{1}{n} + \frac{\pi^2}{6} (n-1) \frac{1}{\nu^2} \\
\quad + \frac{7 \pi^4}{360} (n-1)(n-2)(n-3) \frac{1}{\nu^4} \right]. \quad (A11)
\]
Thus, in the degenerate regime,
\[
\max \left[ g_{3/2} \left( -e^{\beta \mu_a - y} \right) \right] \sim (\frac{1}{\beta \mu_a})^{3/2}. \quad (A12)
\]
One may therefore take as a condition for the expansion of Eq. (A9):
\[
\beta \mu_a \gg \frac{1}{(\beta E_B)^{1/2}}, \quad (A13)
\]
where \( E_B \equiv \hbar^2 / (ma^2) \) is the approximate binding energy of the molecule.

Using the integral relations
\[
g_4(z) = \frac{2}{\sqrt{\pi}} \int_0^\infty dy y^{1/2} g_{5/2}(yz) \quad (A14)
\]
etc., one may resolve the first term in the expansion of Eq. (A9) exactly. An additional useful relation, necessary for calculating the potential energy by integration by parts, is
\[
\int dy \; g_n \left( qe^{-y} \right) = -g_{n+1} \left( qe^{-y} \right). \quad (A15)
\]
To resolve the order \( \alpha \) term of Eq. (A9), one notes that there are two regimes of integration: (a) \( y \ll \beta \mu_a \) and (b) \( y \gg \beta \mu_a \). For a degenerate Fermi gas, so that \( \beta \mu_a \gg 1 \), the two leading contributions to the integrals are obtained in regime (a). Therefore, in order to find the result to order \( (T/T_F)^2 \), for which the two leading order terms are required, it suffices to perform the integral by the use of the expansion given in Eq. (A11). Expanding around small \( y \) and integrating, one obtains a final result similar to Eqs. (A13) - (A20) but dependent on the chemical potential \( \mu_a \).

To obtain a self-consistent correction, the relation between the chemical potential and the Fermi temperature can be calculated from the equation for the total number of fermions
\[
N = n_s \int \frac{d^3r d^3p}{(2\pi)^3} \nu(r, p), \quad (A16)
\]
where \( n_s = 2 \) is the number of spin states. One finds, by the same methods as outlined above, that
\[
\frac{\mu}{k_B T_F^0} = \left( 1 - \frac{512}{315 \pi^2} k_F^0 |a| \right) \\
\quad - \left( \frac{\pi^2}{3} + \frac{16}{315} k_F^0 |a| \right) \left( \frac{T}{T_F} \right)^2 \quad (A17)
\]
to second order in \( T/T_F^0 \) and first order in \( k_F^0 |a| \). Eliminating the chemical potential from the equations for the energies via substitution of Eq. (A17), one obtains Eqs. (A13) - (A20).

**APPENDIX B: CORRECTION TO THE ENTROPY FOR A WEAKLY INTERACTING FERMI GAS**

Equation (24) may be conveniently rearranged as
\[
S = 2k_B \sum_{r, p} \left[ \nu x + \ln(1 + e^{-x}) \right] \quad (B1)
\]
where
\[
x \equiv \beta (E(r, p) - \mu). \quad (B2)
\]
Assuming the semiclassical local density approximation, one can make the change of variables
\[
u \equiv \beta [\mu_a - V(r) - U_{mf}(r)], \quad (B3)
\]
\[
z \equiv \beta \frac{p^2}{2m_a}, \quad (B4)
\]
\[
S = \int d^3r \; S(r). \quad (B5)
\]
Then, integrating the second term in Eq. (B1) by parts, one finds
\[
S(r) = A \int_0^\infty dz \; z^{1/2} \left( z - u \right) - \frac{2 z}{\Gamma + \exp(z - u)}. \quad (B6)
\]
\[
A \equiv \frac{k_B}{2 \pi^2} \left( \frac{2m_a}{\beta h^2} \right)^{3/2} \quad (B7)
\]
This integral may be resolved as a sum of two Bose functions of form \( g_n(x) \), as given in Eq. (24).
APPENDIX C: DEPENDENCE OF THE FUGACITY ON TEMPERATURE IN THE BOLTZMANN LIMIT

In order to calculate the thermodynamic quantities for the atom-molecule mixture at $T > T_{\text{BEC}}^0$ in Secs. IV A 1 and IV A 2, the following perturbative expansions of the fugacities are useful. Starting with Eq. (A10), and including the mean fields, the relations are

$$e^{\beta \mu_n} \simeq \frac{(T_{\text{BEC}}^0)}{T} \left[ \frac{(T_{\text{BEC}}^0)}{T} \right]^3 + \frac{4\sqrt{2} \gamma}{15} \left[ \frac{(T_{\text{BEC}}^0)}{T} \right]^{11/2}$$

for the molecular fugacity and

$$e^{\beta \mu_a} \simeq \frac{\zeta(3)}{2} \frac{N_a}{N_m} \left( \frac{T_{\text{BEC}}^0}{T} \right)^3$$

for the atomic fugacity, where $\gamma \propto \hbar^2 |a|$ is defined in Eq. (83).

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