DILUTE SOLUTIONS OF He^3 IN He^4 AT LOW TEMPERATURES*

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Dilute solutions of He^3 in He^4 at low temperatures have commanded recent interest because of the Fermi liquid properties and the possible superfluid transition associated with the solute. In particular, we refer to theoretical investigations by Bardeen, Baym, and Pines[1] (BBP), and by Emery.[2] The problem appears particularly suitable for an application of the method of correlated basis functions (CBF). We shall present here an outline of such a microscopic calculation, as well as some preliminary results.

The system under consideration consists of n_4 He^4 atoms and n_3 He^3 atoms in a unit volume, $n_3+n_4=n$, $x=n_3/n \ll 1$, interacting pairwise via the usual Lennard-Jones 6-12 potential $v(r)$, with its strength and range determined by the de Boer–Michels parameters. The Hamiltonian is given by

$$H=\sum_{i=1}^{n_4}\frac{-\hbar^2}{2m_4}\nabla_i^2+\sum_{i=1}^{n_3}\frac{-\hbar^2}{2m_3}\nabla_i^2+\sum_{i<j=1}^{n}v(r_{ij}). \tag{1}$$

On account of the strong repulsion in $v(r)$, short-range correlations are important. In the CBF, one begins by constructing properly symmetrized wave functions which contain correlation factors that vanish at short range. A complete set of such correlated functions can then be used as a basis for computing matrix elements of H and 1. Properties of the ground state and low excited states may then be calculated by approximately diagonalizing these matrices. The CBF corresponding to these states must be physically motivated.

Following Baym, we first separate H into two parts,

$$H=H_0+H_1,$$

$$H_0=\sum_{i=1}^{n}\frac{-\hbar^2}{2m_4}\nabla_i^2+\sum_{i<j=1}^{n}v(r_{ij}),$$

$$H_1=\frac{m_4-m_3}{m_3}\sum_{i=1}^{n_3}\frac{-\hbar^2}{2m_4}\nabla_i^2=\frac{1}{3}\sum_{i=1}^{n_3}\frac{-\hbar^2}{2m_4}\nabla_i^2. \tag{2}$$

H_1 describes the additional zero-point motion due to the replacement of n_3 He^4 atoms by He^3 atoms. It includes only n_3 one-particle operators, and may be regarded as a small correction to H_0. The bulk properties of the solution are dominated by H_0, which is immediately recognized as the Hamiltonian for a system of n He^4 atoms. The wave functions we seek must however be appropriate for n_3 fermions and n_4 bosons. A natural choice of the basis consists of the eigenstates of H_0 with this rather peculiar symmetry. These eigenstates cannot be readily determined. One might, as a first approximation, neglect the symmetry requirement and employ a completely symmetric basis. This means using a good liquid-He^4 ground-state wave function $\psi_0^B(1,2,\cdots,n)$ to evaluate the unperturbed energy

$$E_0^B=\langle\psi_0^B,H\psi_0^B\rangle/\langle\psi_0^B,\psi_0^B\rangle. \tag{3}$$

The first-order perturbation correction is then given by $\langle\psi_0^B,H_1\psi_0^B\rangle/\langle\psi_0^B,\psi_0^B\rangle$. We have however chosen to carry out a more elaborate calculation with a properly symmetrized set of basis functions. The separation of the Hamiltonian in Eq. (2) is used merely to furnish physical motivations in the construction of these functions and mathematical convenience in the subsequent computation of matrix elements. If a perturbation theory is used next, H will be separated in a different manner, the unperturbed part $\mathcal{H}_0$ containing only diagonal matrix elements and the perturbation $\Delta\mathcal{H}$ only nondiagonal matrix elements. H_0 and H_1 both contribute to $\mathcal{H}_0$ and to $\Delta\mathcal{H}$.

For the ground state, H_0 suggests a trial wave function of the form

$$\Psi_0=\psi_0^B(1,2,\cdots,n)\Phi_0(1,2,\cdots,n_3), \tag{4}$$

where ψ_0^B is as defined earlier, for ALL n

atoms, and Φ_0 is a Slater determinant

$$\sum_\mu (\pm)\frac{P_\mu \phi_0(1,2,\cdots,n_3)}{(n_3!)^{1/2}}, \quad \phi_0=\prod_{i=1}^{n_3}\varphi_{\vec{\mathrm{k}}_i\sigma_i}(i),$$

of n_3 single-particle orbitals $\varphi_{\vec{\mathrm{k}}_i\sigma_i}(i)$, here taken as plane waves multiplied by spin functions. Ψ_0, as required, is antisymmetric with respect to the interchange of two atoms labeled 1 through n_3, and symmetric with respect to the interchange of two atoms labeled n_3+1 through n. The presence of $\psi_0{}^B$ implies that Ψ_0 accounts properly for the short-range correlations for each pair of atoms.

For the excited states, we note that there should be two branches of excitation: The phonon (-roton) spectrum of pure He^4 will be somewhat modified by the presence of the impurities, and the free Fermi gas excitations of He^3 will be modified by the He^3-He^3 interactions as well as interactions of He^3 atoms with the He^4 background. A suitable basis will therefore contain functions describing (a) states with no phonons and a distribution of fermions excited out of the Fermi Sea, (b) states with one or more phonons and a filled Fermi Sea, and (c) states with both phonons and excited fermions. Free phonon states for pure He^4 may be described[3] by

$$\psi^{B\,m_1,m_2,\cdots,m_\nu}_{\vec{\mathrm{k}}_1,\vec{\mathrm{k}}_2,\cdots,\vec{\mathrm{k}}_\nu}(1,2,\cdots,n)$$

$$=\prod_{j=1}^{\nu}\left[\frac{\rho_{\vec{\mathrm{k}}_j}}{[ns(k_j)]^{1/2}}\right]^{m_j}\psi_0{}^B(1,2,\cdots,n),$$

where

$$\rho_{\vec{\mathrm{k}}}=\sum_{i=1}^{n}\exp(i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}_i)$$

is the density-fluctuation operator and $S(k)$ is the liquid structure function at density n. m_j is the number of phonons with momentum $\vec{\mathrm{k}}_j$ present. The free Fermi gas states are simply Slater determinants

$$\Phi_{\vec{\mathrm{k}}_1\sigma_1,\vec{\mathrm{k}}_2\sigma_2,\cdots,\vec{\mathrm{k}}_{n_3}\sigma_{n_3}}(1,2,\cdots,n_3)$$

like Φ_0, with specified momentum and spin quantum numbers. Our correlated basis is constructed from the products of these two types of well-defined functions, and has the required symmetry property. This basis is admittedly not orthogonal, but our previous experiences with the application of CBF to pure He systems[4,5] lead us to beleive that the orthogonalization is by far easier for dilute solutions. On the other hand, the evaluation, second quantization, and diagonalization of the H matrix are much more difficult. We are currently engaged in these calculations; details will be presented in future reports. In this paper we shall report on results of a first-order perturbation calculation, which is, of course, also variational. Several properties of the solution have been numerically deduced from this calculation. They are in good quantitative agreement with experiments, and with results of phenomenological or model calculations.

To first order, the ground-state energy E_0 of the system is given by

$$E_0\approx\langle H_0\rangle+\langle H_1\rangle,$$
$$\langle H_0\rangle=\langle\Psi_0,H_0\Psi_0\rangle/\langle\Psi_0,\Psi_0\rangle,$$
$$\langle H_1\rangle=\langle\Psi_0,H_1\Psi_0\rangle/\langle\Psi_0,\Psi_0\rangle. \tag{5}$$

$\langle H_0\rangle$ is evaluated using a modified version of the Wu-Feenberg cluster development.[6] It results in the following series:

$$\langle H_0\rangle=E_0{}^B+xE_{01}(x)+x^2E_{02}(x)+x^3E_{03}(x)+\cdots, \tag{6}$$

with $E_0{}^B$ given in Eq. (3) and

$$E_{01}(x)=\tfrac{3}{5}ne_{\mathrm{F}}{}^{(4)},$$

$$E_{02}(x)=24ne_{\mathrm{F}}{}^{(4)}\int_0^1[S(2k_{\mathrm{F}}r)-1][1-\tfrac{3}{2}r+\tfrac{1}{2}r^3]r^4dr,$$

$$E_{03}(x)=-\left(\frac{3}{8\pi}\right)^3ne_{\mathrm{F}}{}^{(4)}\iiint_{\text{unit sphere}}r_{12}{}^2S(k_{\mathrm{F}}r_{12})[S(k_{\mathrm{F}}r_{23})-1][S(k_{\mathrm{F}}r_{31})-1]d\vec{\mathrm{r}}_1d\vec{\mathrm{r}}_2d\vec{\mathrm{r}}_3, \tag{7}$$

$$k_{\mathrm{F}}{}^3=3\pi^2nx,$$

$$e_{\mathrm{F}}{}^{(4)}=\hbar^2k_{\mathrm{F}}{}^2/2m_4.$$

The expansion is in powers of the He^3 concentration and in the deviation of the liquid structure function from unity. It is expected to converge rapidly. Through integrations by parts and rearranging terms, $\langle H_1\rangle$ may be obtained:

$$\langle H_1\rangle = \langle H_0\rangle_T + \tfrac{1}{3}[xE_{01}(x) + x^2E_{02}(x) + x^3E_{03}(x) + \cdots], \tag{8}$$

where

$$\langle H_1\rangle_T = \int \psi_0{}^B \Phi_0{}^* \phi_0 \left[\sum_{i=1}^{n_3} (-\hbar^2/6m_4)\nabla_i{}^2\right] \psi_0{}^B d\tau_{12\cdots n} \left[\int \psi_0{}^{B^2} \Phi_0{}^* \phi_0 d\tau_{12\cdots n}\right]^{-1}; \tag{9}$$

the integration over τ_i includes a summation over the spin index for $i \leqslant n_3$. The other term in $\langle H_1\rangle$ combines with like terms in $\langle H_0\rangle$, resulting in a numerical factor $\frac{4}{3}$ which has the same effect as redefining $E_{0i}(x)$ in terms of $e_F{}^{(3)} \equiv \hbar^2 k_F{}^2/2m_3$, as expected from the fact that all statistical corrections are due to mass-3 atoms. $\langle H_1\rangle_T$ is evaluated using a modified version of the van Kampen cluster development.[7] The leading term turns out to be $\frac{1}{3}xT_0{}^B$, where $T_0{}^B$ is the ground-state kinetic energy for pure He^4 at density n. This term is, like $E_0{}^B$ in Eq. (6), augmented by a series representing additional statistical corrections which we shall not deal with in detail, for reasons to become clear immediately below.

The numerical evaluation of these expressions is carried out using for $\psi_0{}^B$ the wave function calculated by Massey[4] for a Lennard-Jones 6-12 potential with de Boer-Michels parameters,[8] for a range of densities n and concentrations x. The adequacy of $\psi_0{}^B$ as a solution to the Schrödinger equation for the pure He^4 system is discussed in detail in Refs. 4 and 8. Table I gives $\langle H_0\rangle$ at $x = 6\,\%$. The statistical corrections are indeed rapidly converging, small, and slowly varying. Also given in Table I is the leading term of $\langle H_1\rangle_T$, $\frac{1}{3}xT_0{}^B$, at $x = 6\,\%$. It is smaller than $E_0{}^B$ by a factor of 20. Statistical corrections to this term will be down by at least another two orders of magnitude and can be safely disregarded. The smallness of the effects of symmetry on bulk properties of the solution is easy to understand and was recognized by previous authors. Our calculation here merely substantiates this conclusion with quantitative evidence.

A measure of the effective interactions between two He^3 atoms in the solution can be obtained from the results of Table I. It claims unique importance in the determination of the Fermi-liquid properties and the transition temperature. According to BBP, a velocity- and spin-independent effective potential V_k has a long-wavelength limit proportional to α^2, where α is the fractional increase in the volume of the system resulting from the replacement of a He^4 atom by a He^3 atom:

$$V_0 = -\alpha^2 m_4 s^2/n_4{}^0, \tag{10}$$

s being the velocity of sound in pure He^4 at density $n_4{}^0$. α is given by

$$\alpha = \frac{n_4{}^0}{m_4 s^2} \frac{\partial}{\partial n_4{}^0}\left(\frac{1}{3}\frac{T_0{}^B}{n_4{}^0}\right). \tag{11}$$

This is an approximate result for an opposite-spin pair or near-zero concentration of He^3. In terms of α the density of the solution $n(P)$ at pressure P is given by

$$n_4{}^0(P) = n(P)[1 + \alpha(P)x],$$

Table I. $\langle H_0\rangle$ and $\langle H_1\rangle$ at $x = 6\,\%$.

n (Å^{-3})	$E_0{}^B/n$ (°K)	$xE_{01}(x)/n$ (°K)	$x^2E_{02}(x)/n$ (°K)	$x^3E_{03}(x)/n$ (°K)	$\langle H_0\rangle/n$ (°K)	$\frac{1}{3}\times T_0{}^B/n$ (°K)
0.0218	−5.853	0.0249	−0.0007	−0.00000	5.827	0.281
0.0226	−5.969	0.0255	−0.0007	−0.00000	5.943	0.299
0.0234	−6.027	0.0261	−0.0007	−0.00000	6.000	0.317
0.0242	−6.035	0.0267	−0.0007	−0.00000	6.007	0.336
0.0250	−5.990	0.0273	−0.0007	−0.00000	5.962	0.355
0.0258	−5.715	0.0278	−0.0007	−0.00000	5.686	0.374

or

$$\alpha(P)x=\frac{n_4^0(P)-n(P)}{n(P)}. \qquad (12)$$

Thermodynamic properties of the solution at low temperatures may then be approximately deduced from the knowledge of α as a function of the pressure. Figure 1 shows $\alpha(P)$ obtained in our calculation at $x=6\,\%$, $n_4^0(P)$ and $s(P)$ having been deduced from recent experimental data.[9] At $P=0$, we have $\alpha=0.303$ as compared with the experimental value[10] (at 1.2°K) $\alpha\approx 0.28$. Also, at zero pressure,

$$n_4^0\partial\alpha/\partial n_4^0=-1.4,$$

and

$$\frac{\partial|V_0|}{\partial n_4^0}=-4.5\frac{|V_0|}{n_4^0}.$$

The latter results involve the second derivative of T_0^B with respect to n_4^0. The magnitudes should not be taken seriously. The sign indicates that for fixed concentration, α decreases with increasing pressure; in other words, the difference in the specific volumes of He^4 and He^3 slowly diminishes. The result is consistent with considerations based on known compressibilities of pure helium liquids. Consequently, the effective interaction is seen to be weakened as pressure increases, lowering the transition temperature to below the microdegree range. One might compare these numerical results with those of BBP's hard-sphere-model calculation; they obtained

$$\alpha=0.31,$$

$$n_4^0\partial\alpha/\partial n_4^0=-1.13,$$

and

$$\frac{\partial|V_0|}{\partial n_4^0}\approx-2.8\frac{|V_0|}{n_4^0}.$$

The approximation of the ground-state energy E_0 by $E_0^B+\frac{1}{3}xT_0^B$ is not valid for properties of the mixture which are specifically ascribed to the solute. In the following we subject this approximation to a useful test of accuracy, and show that a most encouraging improvement may be anticipated upon the inclusion of higher order perturbation corrections. Let $\Delta\mu$ be the difference between the chemical potentials of (a) a single He^3 atom in liquid He^4, μ_3^S, and (b) a He^4 atom in pure He^4, μ_4^P. From the experimental data of Edwards and the calculations of Ebner,[11] this number is known to be

$$\Delta\mu_{\rm expt}=\mu_3^S-\mu_4^P\approx 4.30^\circ{\rm K}$$

at $P=0$. Our first-order theory gives

$$\mu_3^S=\left\{\frac{\partial}{\partial n_3}\left[(n_3+n_4)\frac{E_0^B}{n}+\frac{1}{3}n_3\frac{T_0^B}{n}+\cdots\right]\right\}_{x=0}$$

$$=\frac{E_0^B}{n}+\frac{1}{3}\frac{T_0^B}{n},$$

$$\mu_4^P=E_0^B/n,$$

and therefore

$$\Delta\mu_{\rm th}=\frac{1}{3}\frac{T_0^B}{n}=4.77^\circ{\rm K}.$$

The discrepancy between $\Delta\mu_{\rm expt}$ and $\Delta\mu_{\rm th}$ is not insignificant. It is however possible to estimate higher order corrections in the perturbation treatment. Davison[12] has performed a second-order Brillouin-Wigner calculation for a system of one He^3 atom in liquid He^4, using matrix elements describing the absorption or emission of a phonon by the He^3 atom, and an approximate wave function for ψ_0^B calculated earlier by Massey with a different Lennard-Jones potential.[4] He obtained an effective mass for the He^3 atom as well as a constant shift $\mathcal{E}_2$ on the ground-state energy:

$$\mathcal{E}_2\approx-0.57^\circ{\rm K}.$$

At small concentrations, the He^3 atoms will act quite independently, each producing the same shift $\mathcal{E}_2$. Our ground-state energy E_0 of the system is then corrected by the addition

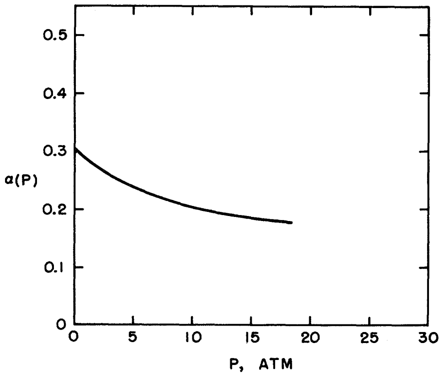

FIG. 1. The BBP parameter α as a function of pressure.

of a term $n_3\mathcal{E}_2$, resulting in

$$\Delta\mu_{\text{th}}=\left[\frac{E_0{}^B}{n}+\frac{1}{3}\frac{T_0{}^B}{n}+\mathcal{E}_2\right]-\left[\frac{E_0{}^B}{n}\right]$$

$$\approx 4.77^\circ\text{K}-0.57^\circ\text{K}=4.20^\circ\text{K},$$

in good agreement with $\Delta\mu_{\text{expt}}$.

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STUDY OF THE Li ION IN KCl USING THE SPIN-PHONON INTERACTION*

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In a crystal which contains magnetic ions, the spin-phonon interaction will modify the normal modes.[1] To a crude approximation, the interaction effectively removes a band of phonons close to the Larmor frequency of the spins. The thermal conductivity, then, will be modified by the absence of these carriers, and by sweeping the magnetic field it should be possible to determine their distribution function. Since this function depends on the phonon-scattering processes in the crystal, this is a potentially useful technique for obtaining phonon mean free paths.[2]

In particular, it has been suggested[3] that it should be possible to study the phonon scattering by a nonmagnetic defect by comparing the thermal conductivity as a function of magnetic field for two crystals: a "pure" crystal containing only the magnetic ions, and another containing, in addition to the magnetic ions, the nonmagnetic defects to be studied. In other words, the magnetic ion is used as a probe to study the nonmagnetic defect.

We wish to report here the first results of such a study of the Li ion in KCl. This defect has been investigated through its effect on the temperature dependence of the thermal conductivity.[4] Briefly, it has been deduced that there is a strong resonant scattering at about 1.2 cm^{-1}. However, theory indicates that the Li ion occupies a position displaced from the center towards the [111] directions in the unit cell.[5] If the potential is isotropic, this should lead to four equally spaced levels.[6] It is not surprising that the temperature dependence of the thermal conductivity does not resolve these since the effective resolution of the "spectrometer" is roughly equal to the frequency. The spin-phonon technique, on the other hand, promises an improvement in resolution: The maximum change in the thermal conductivity on applying a magnetic field is often no more that 10 to 30 %.[7] This indicates that the width of the band of phonons removed from the conduction process is on the order 10 to 30 % of the total. Thus we would expect to have improved the resolution by a factor of between 3 and 10.

The change in thermal conductivity on applying a magnetic field can be written approximately as[3]

$$\Delta K=-AT^3 f(x)\Delta x,$$

where

$$A=k^4/2\pi^2\bar{v}h^3,$$

$$x=h\omega_0/kT=g\beta H/kT,$$

$$f(x)=[e^x/(e^x-1)^2]x^4[\sum 1/\tau(x)]^{-1}.$$

$\tau(x)$ is a relaxation time determined by phonon-scattering processes at zero field, $\bar{v}$ is an aver-