THERMODYNAMICS OF LIQUID ^3He – ^4He MIXTURES

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The osmotic pressure of ^3He – ^4He solutions is shown to follow in a natural way from the separation of the specific heat in a quasiparticle contribution and a ^4He -contribution. Expressions for important thermodynamic properties such as the chemical potentials, the internal energy, the entropy, specific heat, osmotic pressure, etc. are given for the case the quasiparticle gas can be treated as a nearly-ideal Fermi gas. The zero kelvin and the high-temperature limits are tabulated. A first-order approximation is given for the effect of the ^3He quasiparticle contribution to the second-sound velocity in the high-temperature limit.

1. Introduction

In this paper we derive the expressions for thermodynamic functions of state of liquid ^3He – ^4He II mixtures at zero pressure and related quantities such as the osmotic pressure and the velocity of second sound.

The thermodynamics of ^3He – ^4He mixtures was treated before by other authors, see refs. [1–10]. The specific heat of liquid ^3He – ^4He mixtures is often treated as the sum of a pure ^4He contribution and a contribution of a gas of quasiparticles at the same particle density as the ^3He component. We will call this description the quasiparticle description.

In many papers regarding the thermodynamics of ^3He – ^4He mixtures the osmotic pressure seems to be a special property of the ideal Fermi-particle gas, with an unclear physical meaning in nonideal cases. In the second paragraph of this paper it will be shown that the osmotic pressure is a natural consequence of the separation of the

specific heat in a pure ^4He -contribution and a quasiparticle contribution. We hope that this approach will be clarifying in several ways.

At present, it is generally assumed that the quasiparticles are Fermi particles with a nearly-quadratic excitation spectrum. The deviations of the quadratic spectrum are assumed to be small. We will call the gas a *nearly*-ideal Fermi gas. When the deviations from the quadratic excitation spectrum at a given concentration are neglected we will call the gas an ideal Fermi gas.

In the third paragraph relations for the internal energy, the specific heat, the entropy, the osmotic pressure, and the other important thermodynamic quantities will be derived in terms of Fermi functions. The relations are valid at all temperatures. Graphs will be given of the Fermi functions as functions of temperature. The deviations of some thermodynamic quantities from the ideal Fermi-gas behaviour will be expressed in terms of Fermi functions and represented in graphs as well.

From the general relations expressions are derived for the low-temperature and high-temperature limits, which are of practical importance, e.g., for the interpretation of the measurements of the specific heat and second sound of dilute

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mixtures. In our view a consistent derivation is necessary because some derivations in the literature are inconsistent.

2. The quasiparticle description

We write the molar specific heat of the mixture C_m in the form:

$$C_m(T, x) = xC_q(T, x) + (1 - x)C_4^0(T). \quad (1)$$

In this equation x is the molar ^3He concentration and C_4^0 is the molar specific heat of pure ^4He at constant volume.

In this paper, the superscript 0 refers to a pure substance. The subscripts 3 and 4 refer to ^3He and ^4He , respectively. Molar quantities of the solution are denoted with a lower index m. Quantities applying to one mole of quasiparticles get a lower index q. In cases where the quasiparticle gas is considered to be an *ideal* Fermi gas we use a lower index F. The corresponding quantities for the nearly ideal Fermi gas are denoted with an additional prime. As the discussion is limited to the fluid properties at zero pressure, the pressure dependences will not be given explicitly, except for the relations where the osmotic pressure is introduced.

Equation (1) can be regarded as defining C_q . It contains all contributions to the specific heat which are not included in the $(1 - x)C_4^0$ term. In this section we will not specify the nature of the quasiparticles. The model, in which the quasiparticle gas is treated as a nearly-ideal Fermi gas, will be introduced in the next section.

In the discussion given here C_q is treated as the specific heat of a quasiparticle gas at the same particle density as the ^3He component. In order to emphasize this aspect one could write the dependence of C_q on x as the dependence on the molar volume V_q of the quasiparticles: $C_q(T, x) = C_q(T, V_q)$, where

$$V_q(x) = V_m(x)/x \quad (2)$$

is equal to the volume containing one mole of ^3He (or equivalently one mole of quasiparticles).

The molar volume V_m of the solution is given by

$$V_m(x) = V_4^0(1 + \alpha x) \quad (3)$$

where V_4^0 is the volume per mole of pure ^4He and α is a constant [11]. The molar volume V_m will be considered to be pressure and temperature independent.

Due to the validity of the third law, S_m at 0 K is independent of x . Therefore the entropy of the solution S_m can be calculated as a function of T and x by a single integration from $T = 0$ to T of C_m/T at constant x . We put the entropies at 0 K equal to zero. The result is:

$$S_m(T, x) = xS_q(T, V_q) + (1 - x)S_4^0(T), \quad (4)$$

where S_q represents the entropy of the quasiparticles given by

$$S_q(T, V_q) = \int_0^T \frac{C_q(T', V_q)}{T'} dT', \quad (5)$$

and S_4^0 is the molar entropy of pure ^4He .

The internal energy U_m can be obtained from eq. (1) by integration over T , and gives:

$$U_m(T, x) = U_m(0, x) + x[U_q(T, V_q) - U_q(0, V_q)] + (1 - x)[U_4^0(T) - U_4^0(0)]. \quad (6)$$

where

$$U_q(T, V_q) = U_q(0, V_q) + \int_0^T C_q(T', V_q) dT' \quad (7)$$

and U_4^0 represent the internal energies of the quasiparticle gas and pure ^4He , respectively.

From eqs. (4) and (6) only differences between thermodynamic quantities at temperature T and $T = 0$, at a given concentration can be calculated. In the specification of the properties of the quasiparticles we still have to fix $U_q(0, V_q)$, the zero point of the energy. It will be taken in such a way that

$$U_m(0, x) = xU_q(0, V_q) + (1 - x)U_4^0(0). \quad (8)$$

This means that eq. (6) obtains the form

$$U_m(T, x) = xU_q(T, V_q) + (1 - x)U_4^0(T). \quad (9)$$

We will take the internal energies of the pure components at zero kelvin equal to zero: $U_3^0(0) = 0$, and $U_4^0(0) = 0$. In this case

$$U_m(0, x) = U_m^E(0, x), \quad (10)$$

where U_m^E is the excess internal energy per mole solution.

The molar Gibbs free energy G_m follows from $G_m = U_m + pV_m - TS_m = U_m - TS_m$. With (4) and (9)

$$G_m = G_4^0(T) + x(F_q(T, V_q) - G_4^0(T)), \quad (11)$$

where G_4^0 is the Gibbs free energy of pure ^4He , and F_q is the free energy of the quasiparticles. The ^4He chemical potential follows from:

$$\mu_4 = G_m - x \left(\frac{\partial G_m}{\partial x} \right)_T \quad (12)$$

and relation (11):

$$\mu_4(T, x) = G_4^0(T) - x^2 \left(\frac{\partial F_q(T, V_q)}{\partial x} \right)_T. \quad (13)$$

We now use the relation:

$$dF_q = -S_q dT - p_q dV_q, \quad (14)$$

which in fact defines the pressure $p_q(T, V_q)$ as the pressure of the quasiparticle gas. Applying this relation to eq. (13) gives

$$\mu_4(T, x) = G_4^0 - p_q V_4^0. \quad (15)$$

Equation (15) shows that the chemical potential of pure ^4He at zero pressure is equal to the ^4He chemical potential in the solution at the pressure p_q , so pure ^4He at zero pressure is in equilibrium with the solution at pressure p_q .

The osmotic pressure Π of the mixture can be defined by the relation:

$$\mu_4(p, T, x) = G_4^0(p - \Pi, T). \quad (16)$$

In eq. (16) we have written the pressure dependence of the chemical potentials explicitly. At low values of Π , where the pressure dependence

of V_4^0 can be neglected, the right hand side yields:

$$\mu_4(p, T, x) = G_4^0(p, T) - \Pi(T, x)V_4^0. \quad (17)$$

Comparing eq. (15) with eq. (17) shows that the osmotic pressure can be identified with the pressure of the quasiparticle gas:

$$\Pi(T, x) = p_q(T, V_q). \quad (18)$$

In a similar way an expression for μ_3 can be derived resulting in:

$$\mu_3(T, x) = G_q(T, V_q) - p_q V_3. \quad (19)$$

The ^3He partial volume $V_3 = V_4^0(1 + \alpha)$. Equation (19) implies that G_q is equal to the ^3He chemical potential μ_3 in a solution at a pressure p_q [2].

Equations (15) and (19) are consistent with the Gibbs-Duhem relation

$$x d\mu_3 + (1 - x) d\mu_4 = -S_m dT + V_m dp, \quad (20)$$

as can be verified by substitution, and using $(\partial G_q / \partial p_q)_T = V_q$.

Equation (20), applied at $T = 0$ and $p = 0$, with eqs. (15) and (18) gives:

$$\mu_3(0, x) = V_4^0 \int_{x_0}^x \frac{1 - x'}{x'} \cdot \frac{d\Pi_0}{dx'} \cdot dx'. \quad (21)$$

In this equation x_0 is the concentration of the dilute saturated solution at 0 K. The chemical potentials of pure ^3He and ^4He are zero at 0 K, so $\mu_3(0, x_0) = G_3^0(0) = U_3^0(0) = 0$ and $G_4^0(0) = 0$.

In eq. (21) $\Pi_0(x)$ is the osmotic pressure at 0 K. It is related to the excess internal energy through eqs. (10), (12) and (17), keeping in mind that $G_m = U_m$ at $T = 0$.

The osmotic pressure at nonzero temperatures, and the other thermodynamic quantities can thus be calculated from the excess internal energy (or the osmotic pressure at zero temperature) and the specific heat of the quasiparticle gas.

The excess enthalpy H^E is defined as:

$$H^E(T, x) = H_m(T, x) - xH_3^0(T) - (1-x)H_4^0(T), \quad (22)$$

where H_m is the molar enthalpy of the solution, and H_3^0 and H_4^0 are the molar enthalpies of pure ^3He and ^4He , respectively. The excess enthalpy plays an important role in experiments where the two pure components are mixed, and in the comparison between the calculations and the experiment [12, 13].

Conservation of energy of adiabatic ^3He flow through ^4He II [2], leads to

$$H_3^{\text{os}} = \text{constant}, \quad (23)$$

where H_3^{os} is given by

$$H_3^{\text{os}}(T, x) = \mu_3 + \frac{TS_m}{x}. \quad (24)$$

It is called the osmotic enthalpy per mole ^3He . For low temperatures and not too low ^3He concentrations the ^4He contribution in the entropy is negligible.

3. The nearly-ideal Fermi gas

The separation of the mixture specific heat as represented by eq. (1), with C_q equal to the specific heat of a Fermi gas, is based on the theory of Pomeranchuk [14]. In its simplest form the single-particle excitation spectrum is parabolic, as given by Landau and Pomeranchuk [15]. In this case one can apply the familiar ideal-Fermi-gas statistics at a given fixed concentration. It was shown to be correct to order x for the first time by De Bruyn Ouboter et al. [16].

The excitation spectrum of the Fermi particles and their effective mass can be determined from measurements of the specific heat, the osmotic pressure, second sound, the normal-component density, and neutron scattering. It turned out that the excitation spectrum of the ^3He quasiparticles is slightly non-parabolic (see, e.g., refs. [2, 3, 5, 17–19, 10]).

We will continue our discussion of the thermodynamic properties of ^3He - ^4He mixtures of the previous section by introducing the assumption that the quasiparticles constitute a nearly-ideal gas of Fermi particles. The lower index q has to be replaced by a lower index F and a prime.

Guggenheim [20] has treated the thermodynamics of two-component mixtures. For a treatment of the thermodynamics of the ideal Fermi gas the reader is referred to the work of Stoner [21] and to the book of Huang [22].

To second order in k^2 the excitation spectrum is represented by:

$$\varepsilon(x, k) = \varepsilon_0(x) + \varepsilon'_F(x, k), \quad (25)$$

with

$$\varepsilon'_F(x, k) = \frac{\hbar^2 k^2}{2m^*(x)} (1 + \gamma k^2), \quad (26)$$

where m^* is the effective quasiparticle mass at concentration x , k is the magnitude of the wave vector, $\hbar$ is Planck's constant divided by 2π and $\varepsilon_0(x)$ the potential energy of the quasiparticles. The form of the excitation spectrum given by eq. (26) was proposed by Brubaker et al. [23]. The parameter γ is a measure for the nonparabolicity of the excitation spectrum. The presently accepted value is about $-0.08 \text{ \AA}^2$ [24].

As eq. (26) is a development of ε to second order in k^2 , there is no point in expressing derived quantities to higher than first order in γ . The validity of the relations is limited accordingly.

The density of states $n'_F(\varepsilon, \varepsilon_0)$, derived from eqs. (25) and (26), is given by:

$$n'_F(\varepsilon, \varepsilon_0) = n_F(\varepsilon - \varepsilon_0) \left(1 + \frac{\varepsilon - \varepsilon_0}{k_B T_g} \right) \quad \text{for } \varepsilon \geq \varepsilon_0$$

and

$$n'_F(\varepsilon, \varepsilon_0) = 0 \quad \text{for } \varepsilon < \varepsilon_0, \quad (27)$$

with

$$n_F(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}, \quad (28)$$

where V is the volume of one mole of quasiparticles or one mole of ^3He . It is similar to V_q in the previous section and should be denoted as V'_F to be fully consistent with the notation in the present section. However, we prefer to write this volume as V in order to avoid a too cumbersome notation. In eq. (27) we introduced a characteristic temperature T_g defined by:

$$T_g(x) = \frac{-\hbar^2}{5\gamma m^* k_B}, \quad (29)$$

where k_B is Boltzmann's constant. The value of T_g is weakly concentration dependent, due to its dependence of m^* . Typically it is on the order of 10 K. Furthermore we introduce a parameter g :

$$g(x) = -T_F/T_g. \quad (30)$$

In this discussion T_F is the Fermi temperature of the ideal Fermi gas given by

$$T_F(x) = \frac{\hbar^2}{2m^* k_B} \left(3\pi^2 \frac{N_A}{V} \right)^{2/3}. \quad (31)$$

Here N_A is Avogadro's number. The value of T_F of a 1% mixture is about 100 mK, and varies approximately as $x^{2/3}$. Typically $g \approx -0.01$.

The parameter g can be rewritten as

$$g = \frac{5}{2}\gamma \left(\frac{3\pi^2 N_A}{V} \right)^{2/3}, \quad (32)$$

which shows that g is related to the ratio of γ and square of the average particle distance.

The number of ^3He quasiparticles N_A is given by

$$N_A = \int_0^\infty \frac{n'_F(\epsilon, 0) d\epsilon}{1 + \exp(\beta\epsilon - \eta'_F)}. \quad (33)$$

Here $\beta = 1/k_B T$ and η'_F is the reduced chemical potential, defined by:

$$\eta'_F = (\mu'_F - U_0)/RT, \quad (34)$$

where R is the molar gas constant, μ'_F is the chemical potential per mole of ^3He , and $U_0 =$

$N_A \epsilon_0$ is the potential energy of one mole of quasiparticles. The Fermi functions $F_n(\eta)$ with $n > -1$ are defined by

$$F_n(\eta) = \int_0^\infty \frac{x^n}{1 + \exp(x - \eta)} dx. \quad (35)$$

Graphs of the Fermi functions which are of importance to this paper are given in fig. 1. Using definition eq. (35), and the other relations given above, we obtain from eq. (33):

$$1 = \frac{3}{2} t^{3/2} \cdot [F_{3/2}(\eta'_F) - g t F_{5/2}(\eta'_F)]. \quad (36)$$

The parameter t represents the reduced temperature defined by

$$t = T/T_F. \quad (37)$$

The reduced chemical potential η_F of the ideal Fermi gas is determined by eq. (36) with $g = 0$:

$$1 = \frac{3}{2} t^{3/2} \cdot F_{3/2}(\eta_F). \quad (38)$$

In eq. (36) the argument η'_F of the function $F_{3/2}$

Fig. 1. Dependences of the Fermi functions F_n (eq. (35)), as functions of the reduced temperature t , for n values of $\frac{5}{2}$, $\frac{3}{2}$, $\frac{1}{2}$ and $-\frac{1}{2}$, respectively. The values of n are indicated in the figure.

may be replaced by η_F as we are interested only in a first order approximation in g . With eqs. (36), (38), and using the general relationship between Fermi functions:

$$dF_n/d\eta = nF_{n-1} \quad (39)$$

we get:

$$\eta'_F = \eta_F + 2gt \left(\frac{F_{\frac{3}{2}}}{F_{-\frac{1}{2}}} \right)_F, \quad (40)$$

so in general to first order in g :

$$F_n(\eta'_F) = \left(F_n + 2gt \cdot nF_{n-1} \cdot \frac{F_{\frac{3}{2}}}{F_{-\frac{1}{2}}} \right)_F. \quad (41)$$

The lower index F of the brackets in eqs. (40) and (41) indicates that the argument of the Fermi functions is η_F instead of η'_F . As can be deduced from eq. (38) η_F is a function of t only. Note that eq. (39) only holds for $n > 0$. For $n = -\frac{1}{2}$ the derivative exists but it cannot be expressed in terms of Fermi functions.

The product $gt = -T/T_g$ is equal to 5 times the parameter G as introduced by Bowley [9]. It plays an important role in the discussion to follow. In low-concentration specific heat measurements gt is typically in the range -0.001 to -0.1 .

The internal energy per mol quasiparticles is given by

$$U'_F = \int_0^\infty \frac{\epsilon n'_F(\epsilon, 0) d\epsilon}{1 + \exp(\beta\epsilon - \eta'_F)}. \quad (42)$$

With the density of states given by eq. (27) and using eqs. (30), (31) and (37):

$$U'_F(t, x) = U_0 + \frac{3}{2}RT_F t^{5/2} [F_{\frac{3}{2}}(\eta'_F) - gtF_{\frac{3}{2}}(\eta'_F)]. \quad (43)$$

The pressure satisfies:

$$p'_F V = k_B T \int_0^\infty n'_F(\epsilon, 0) \ln[1 + \exp(\eta'_F - \beta\epsilon)] d\epsilon. \quad (44)$$

Integration by parts results in:

$$p'_F V = RT_F t^{5/2} [F_{\frac{3}{2}}(\eta'_F) - \frac{3}{5}gtF_{\frac{3}{2}}(\eta'_F)]. \quad (45)$$

With eqs. (34) and (40) the chemical potential $\mu'_F = G'_F$ can be calculated. Using the general relation $G = U + pV - TS$ and using eqs. (34)–(45), the thermodynamic functions of state can be calculated. The expressions for the ideal gas can be obtained putting $g = 0$ (and hence $\eta'_F = \eta_F$) in these equations. The differences between the expressions for the nearly-ideal gas and the ideal gas are to first order proportional to g , and are tabulated in table I.

Figure 2 represents the deviations from the ideal-gas behaviour of the specific heat and the osmotic pressure.

4. The low-temperature and the high-temperature limiting cases

Near $T = 0$ it holds that $\eta_F \approx 1/t$ and $F_n = 1/[(n+1)t^{n+1}]$. With this result the 0 K values of the thermodynamic functions of state discussed in the previous paragraph can be calculated (table I).

Many measurements of the specific heat and the velocity of second sound are performed in the high-temperature regime, hence in the concentration and temperature region where $t \gg 1$ but still $|gt| \ll 1$. In this region one may apply the general relations given above in the high temperature limit. In this limit the Fermi functions satisfy the relation

$$F_n = nF_{n-1}, \quad (46)$$

so eq. (40) gives:

$$\eta'_F \approx \eta_F + \frac{3}{2}gt. \quad (47)$$

The quasiparticle internal energy is given by:

$$U'_F(t, x) \approx U_0 + \frac{3}{2}RT_F t(1 + Bt^{-3/2} - gt) \quad (48)$$

where $B = 1/\sqrt{(18\pi)}$ gives the first order term in the high temperature expansion of the internal

Table I

Summary of the deviations from the ideal Fermi-gas behaviour, giving the general expressions, the zero temperature values and the high temperature limits, respectively.

Function	Expression	Zero- T value	High- T value
$\frac{\mu'_F - \mu_F}{gRT_F}$	$2t^2 \left(\frac{F_{\frac{3}{2}}}{F_{-\frac{1}{2}}} \right)_F$	$\frac{2}{3}$	$\frac{3}{2}t^2$
$\frac{U'_F - U_F}{gRT_F} \equiv \mathcal{U}$	$t^2 \left(\frac{3F_{\frac{3}{2}}}{F_{-\frac{1}{2}}} - \frac{F_{\frac{5}{2}}}{F_{\frac{1}{2}}} \right)_F$	$\frac{6}{35}$	$-\frac{3}{2}t^2$
$\frac{(p'_F - p_F)V}{gRT_F}$	$t^2 \left(\frac{2F_{\frac{3}{2}}}{F_{-\frac{1}{2}}} - \frac{2F_{\frac{5}{2}}}{5F_{\frac{1}{2}}} \right)_F$	$\frac{8}{35}$	$\frac{9}{4}Bt^{1/2}$
$\frac{S'_F - S_F}{gR}$	$t \left(\frac{3F_{\frac{3}{2}}}{F_{-\frac{1}{2}}} - \frac{7F_{\frac{3}{2}}}{5F_{\frac{1}{2}}} \right)_F$	0	$-3t$
$\frac{F'_F - F_F}{gRT_F}$	$t^2 \left(\frac{2F_{\frac{5}{2}}}{5F_{\frac{1}{2}}} \right)_F$	$\frac{8}{35}$	$\frac{3}{2}t^2$
$\frac{C'_F - C_F}{gR}$	$d\mathcal{U}/dt$	0	$-3t$
$\frac{\rho_{03}V - M^*}{gM^*}$	$-\frac{4}{3}t \left(\frac{F_{\frac{3}{2}}}{F_{\frac{1}{2}}} \right)_F$	$-\frac{4}{3}$	$-2t$

Fig. 2. Corrections of the ideal-Fermi gas values of the osmotic pressure and the specific heat due to the nonparabolic density of states. See table I. (a) Plot of $\Delta p \equiv (p'_F - p_F)V/(gRT_F)$ as a function of t . (b) Plot of $-\Delta C \equiv -(C'_F - C_F)/(gR)$ as a function of t .

energy of the ideal Fermi gas. The high-temperature limits of the deviation of the ideal-gas functions of state are given in table I.

The temperature derivative of eq. (48) gives C'_F :

$$C'_F \approx \frac{3}{2}R(1 - \frac{1}{2}Bt^{-3/2} - 2gt) \\ = \frac{3}{2}R\left(1 - \frac{1}{2}Bt^{-3/2} + \frac{2T}{T_g}\right). \quad (49)$$

This equation shows that in the high-temperature limit the specific heat increases with temperature [16, 5, 19, 10]. The slope is a direct measure of T_g , and hence of γ [25, 26].

Using the value of the osmotic pressure of the nearly-ideal Fermi gas in the high temperature limit as given in table I and the relation $p_F V = 2(U_F - U_0)/3$, we obtain:

$$p'_F = \frac{RT}{V} \left(1 + Bt^{-3/2} + \frac{9}{4}gBt^{-1/2}\right). \quad (50)$$

For $t \gg 1$ this equation gives Van 't Hoff's relation. Ebner [27], has derived an expression for the osmotic pressure in the high-temperature limit, extending the work of Bardeen, Baym and Pines [28, 11] to higher temperatures.

5. The velocity of second sound

The velocity of second sound is one of the main sources of information on the Fermi-gas parameters of ^3He [29–31, 5, 17, 32, 6, 9, 24]. However, the general expression for the velocity of second sound is very complicated. As a result it is not easy to see how the various effects contribute to the second-sound velocity. In this paragraph we will try to disentangle this complicated behaviour by treating the various contributions within the framework of this paper and strictly to first order.

The basic equations for the velocities of first sound, u_1 , and second sound, u_2 , are given by Khalatnikov [33]:

$$u_1^2 = (1 + d) \left(\frac{\partial p}{\partial \rho} \right)_T \quad (51)$$

$$u_2^2 = \frac{M_m}{M_4^2} \frac{\rho_s}{\rho_n} \frac{w}{1 + d} \quad (52)$$

where

$$w = S_4^2 \left(\frac{\partial T}{\partial S_m} \right)_x - x \left(\frac{\partial \mu_4}{\partial x} \right)_T \quad (53)$$

and

$$d = \frac{M_m^2}{M_4^2} \frac{\rho_s}{\rho_n} \left(\frac{x}{\rho} \left(\frac{\partial \rho}{\partial x} \right)_T \right)^2, \quad (54)$$

where S_4 is the partial entropy of the ^4He component and u_2 is equal to the velocity of second sound to first order. In these expressions M_m is the molar mass of the mixture, M_4 (M_3) is the ^4He (^3He) molar mass, ρ_s (ρ_n) is the superfluid (normal fluid) density, and ρ is the density of the solution.

From eq. (52), ρ_n can be derived from the measured velocity of second sound, provided the temperature and concentration dependences of w and d are known. The so-called “inertial effective mass” can be obtained from this by subtracting the density of the normal ^4He II component.

Equation (53) can be simplified as follows: $S_4 = -(\partial \mu_4 / \partial T)_x$ so $S_4(\partial T / \partial S_m)_x = -(\partial \mu_4 / \partial S_m)_x$, hence:

$$w = -S_4 \left(\frac{\partial \mu_4}{\partial S_m} \right)_x - x \left(\frac{\partial \mu_4}{\partial x} \right)_T. \quad (55)$$

With

$$\left(\frac{\partial \mu_4}{\partial x} \right)_T = \left(\frac{\partial \mu_4}{\partial x} \right)_{S_m/x} + \left(\frac{\partial \mu_4}{\partial S_m/x} \right)_x \left(\frac{\partial S_m/x}{\partial x} \right)_T \quad (56)$$

and eq. (4) we obtain:

$$w = -x \left(\frac{\partial \mu_4}{\partial x} \right)_{S_m/x}. \quad (57)$$

This expression for w has been derived before by Ghazlan and Varoquaux [34]. Together with eq. (17) it shows very elegantly that second

sound can be considered as an adiabatic osmotic pressure wave [6].

We will now derive the lowest order effects of the x -dependence of the V_m , the x -dependence of m^* , and of the g -dependence of the density of states on the second-sound velocity. We are interested in the contributions of the quasiparticle gas, so we put $S_m/x = S'_F$. In this case we may write:

$$\left(\frac{\partial \mu_4}{\partial x}\right)_{S'_F} = -V_4^0 \left(\frac{\partial p'_F}{\partial x}\right)_{S'_F}. \quad (58)$$

The right hand side can be rewritten using the relation

$$\left(\frac{\partial p'_F}{\partial x}\right)_{S'_F} = \left(\frac{\partial p'_F}{\partial x}\right)_t + \left(\frac{\partial p'_F}{\partial t}\right)_x \left(\frac{\partial t}{\partial x}\right)_{S'_F} \quad (59)$$

or

$$\left(\frac{\partial p'_F}{\partial x}\right)_{S'_F} = \left(\frac{\partial p'_F}{\partial x}\right)_t - \left(\frac{\partial p'_F}{\partial t}\right)_x \left(\frac{\partial t}{\partial S'_F}\right)_x \left(\frac{\partial S'_F}{\partial x}\right)_t. \quad (60)$$

The entropy in the high-temperature limit is given by (table 1) $S'_F = S_F - 3gtR$. We use the fact that S_F is a function of t only, and apply the approximate relation $dg/dx \approx 2g/3x$ (see eqs. (3) and (32)). In this way we obtain:

$$\left(\frac{\partial S'_F}{\partial x}\right)_t = -\frac{2gtR}{x}. \quad (61)$$

This term is in first order proportional to g . As we are interested in terms of first order in g we may replace p'_F by p_F and S'_F by S_F in the second term of eq. (60). As

$$\left(\frac{\partial p_F}{\partial t}\right)_x = \frac{2T_F C_F}{3V} \quad \text{and} \quad \left(\frac{\partial t}{\partial S_F}\right)_x = \frac{t}{C_F}$$

we obtain for the second term in eq. (60)

$$-\left(\frac{\partial p'_F}{\partial t}\right)_x \left(\frac{\partial t}{\partial S'_F}\right)_x \left(\frac{\partial S'_F}{\partial x}\right)_t \approx \frac{4}{3} \frac{T}{V_4^0} gtR. \quad (62)$$

The ^3He -effective mass is given by:

$$m^*(x) = m_0^*(1 + \delta x). \quad (63)$$

Here the parameter δ determines the concentration dependence of the effective mass and m_0^* is the quasiparticle effective mass at zero concentration.

After a little algebra, expressing the first term in α and δ using eqs. (3), (31) and (50), we obtain for w :

$$w = \frac{5}{3} xRT [1 - 2\alpha x - \frac{3}{5} \delta x + Bt^{-3/2} + \frac{4}{5} gt]. \quad (64)$$

Expression (52) contains the normal fluid density ρ_n which also contains a contribution from the ^3He -component. This contribution is given by [35, 5],

$$\rho_{n3} = -\frac{1}{3} \frac{\hbar^2}{\pi^2} \int \frac{\partial f_{FD}}{\partial \epsilon} k^4 dk, \quad (65)$$

where $f_{FD} = [1 + \exp(\beta(\epsilon - \epsilon_0) - \eta'_F)]^{-1}$. After integration by parts, ρ_{n3} can be expressed in Fermi functions according to:

$$\rho_{n3} = \frac{M^*}{V} \left[1 - \frac{4}{3} gt \frac{F_{3/2}}{F_{1/2}} \right]_F \quad (66)$$

with $M^* = m^* N_A$.

Using the high-temperature limiting values of the Fermi functions with eqs. (3) and (63) gives to first order in αx , δx and g :

$$\rho_{n3} = x \frac{M_0^*}{V_4^0} (1 - \alpha x + \delta x - 2gt). \quad (67)$$

Furthermore

$$\begin{aligned} \rho_s &\approx \rho - \rho_{n3} \\ &\approx \frac{M_4}{V_4^0} \left[1 - 0.25x - \alpha x - x \frac{M_0^*}{M_4} \right] \end{aligned} \quad (68)$$

and

$$\frac{M_m}{M_4} = 1 + \frac{M_3 - M_4}{M_4} x = 1 - 0.25x. \quad (69)$$

Finally we note that the parameter d (eq. (54)) is to lowest order equal to:

$$d \simeq x \frac{M_4}{M_0^*} \left[\frac{M_3 - M_4}{M_4} - \alpha \right]^2$$

$$= \frac{M_4}{M_0^*} (\alpha + 0.25)^2 x. \quad (70)$$

Combining the equations given above results in the equation

$$u_2^2 \simeq \frac{5RT}{3M_0^*} \left[1 + Bt^{-3/2} + 2.7gt - 1.6\delta x \right.$$

$$\left. - 2\alpha x - d - 0.5x - \frac{M_0^*}{M_4} x \right]. \quad (71)$$

Equation (71) contains terms due to the Fermi character of the quasiparticles ($Bt^{-3/2}$), the deviation of the ideal-gas excitation spectrum ($4.3gt$), the concentration dependence of the effective mass ($-1.6\delta x$) and the concentration dependence of the molar volume (the α -dependent terms), respectively. It clearly shows the relative importance of each of the contributions.

6. Conclusion

In this paper we showed that the osmotic pressure of ^3He - ^4He solutions follows in a natural way from the separation of the specific heat in a quasiparticle contribution and a ^4He -contribution. Expressions for important thermodynamic quantities of the solutions were derived for the case that the quasiparticle gas can be treated as a nearly-ideal Fermi gas. The first order correction terms were tabulated.

A first-order expression was obtained which shows how the various mixture parameters affect the second-sound velocity.

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