a small change.

We have made no reference to the role that He_4^+ could play in a helium afterglow plasma. Not only is it impossible to predict the pressure dependence of He_4^+/He_2^+ at pressures above 25 Torr[3] but also the electronic-recombination coefficient of He_4^+ is not known. Thus, any comments about He_4^+ would be completely speculative.

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Ground-State Energy of Liquid He^3 and Liquid He^4: Evaluation from the Sound-Propagation Data*

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Recent measurements on the pressure dependence of the sound velocity $c(P)$ in liquid He^3 and liquid He^4 are employed for deriving the ground-state energy of these liquids as power series in the parameter $(\rho-\rho_0)/\rho_0$, where ρ is the density of the liquid while ρ_0 is the value of ρ at saturated vapor pressure. Results thus obtained are compared with the corresponding ones derived theoretically. The existence of an almost *linear* relationship between the variables c and ρ, as observed by Aziz *et al.* on one hand and by Abraham *et al.* on the other, is discussed.

I. INTRODUCTION

Experimental determination of the pressure dependence of the sound velocity $c(P)$ and density $\rho(P)$ in liquid He^3 and liquid He^4 has been reported recently.[1,2] The measurements have been carried out at 150 mK in the case of He^3 and at 100 mK in the case of He^4. At such low temperatures, isothermal and isentropic processes are almost identical. We may, therefore, write

$$c^2=\left(\frac{\partial P}{\partial \rho}\right)_S=\frac{1}{m}\left\{\frac{\partial}{\partial \rho}\left[\rho^2\left(\frac{\partial E}{\partial \rho}\right)_S\right]\right\}_S$$

$$\simeq\frac{1}{m}\left\{\frac{\partial}{\partial \rho}\left[\rho^2\left(\frac{\partial E}{\partial \rho}\right)_T\right]\right\}_T . \qquad (1)$$

Here, E denotes the energy per particle of the system while m denotes the particle mass. In view of the fact that the velocity of sound varies very little over the temperature range 0–150 mK, the observed data on sound propagation may be employed to derive, with the help of (1), the ground-state energy of the system.

Such an analysis for liquid He^4 has been carried out by Roach *et al.*,[3] who employed the relationship

$$E(\rho)-E(\rho_0)=m\int_{\rho_0}^{\rho}\left[P(\rho')/\rho'^2\right]d\rho' \qquad (2)$$

and expressed their integrated results in the form

$$E(\rho)=E(\rho_0)+a_2\left(\frac{\rho-\rho_0}{\rho_0}\right)^2+a_3\left(\frac{\rho-\rho_0}{\rho_0}\right)^3 . \qquad (3)$$

For liquid He^4 they obtained $a_2 = 13.65$ °K and $a_3 = 7.67$ °K. The corresponding theoretical values derived from the work of Massey and Woo[4] were $a_2=(16.0\pm 0.6)$ °K and $a_3=(10.2\pm 4.5)$ °K, while similar values derived from the work of Schiff and Verlet[5] were $a_2=(14.9\pm 0.4)$ °K and $a_3=(2.6\pm 2.8)$ °K.

One could follow the same approach, as of Roach *et al.*, for determining the ground-state energy of liquid He^3. However, we have preferred to adopt a procedure that enables us to determine the coefficients appearing in the power series

$$E(\rho)=E_0+a_2\left(\frac{\rho-\rho_0}{\rho_0}\right)^2+a_3\left(\frac{\rho-\rho_0}{\rho_0}\right)^3$$

$$+a_4\left(\frac{\rho-\rho_0}{\rho_0}\right)^4+a_5\left(\frac{\rho-\rho_0}{\rho_0}\right)^5+\dots \qquad (4)$$

directly from the coefficients appearing in the series

$$c(\rho)=c_0+c_1\left(\frac{\rho-\rho_0}{\rho_0}\right)^1+c_2\left(\frac{\rho-\rho_0}{\rho_0}\right)^2+c_3\left(\frac{\rho-\rho_0}{\rho_0}\right)^3+\ldots\ . \qquad (5)$$

This procedure not only obviates the integration process encountered by Roach *et al.* but also leads to more accurate values for the desired coefficients. We have applied this procedure for analyzing data on both liquid He^3 and liquid He^4 and have determined, in each case, coefficients a_2–a_5. Comparison with theory, wherever possible, is carried out.

II. PROCEDURE AND RESULTS

Our approach involves a direct use of the thermodynamic formula (1), at 0 °K, in conjunction with the series (4) and (5). This leads to the following hierarchy of relationships:

$$c_0=(2a_2/m)^{1/2}\ , \qquad (6a)$$

$$c_1/c_0=\tfrac{3}{2}(a_3/a_2)+2\ , \qquad (6b)$$

$$c_2/c_0=3(a_4/a_2)-\tfrac{1}{2}[\tfrac{3}{2}(a_3/a_2)-1]^2\ , \qquad (6c)$$

$$c_3/c_0=5(a_5/a_2)-2(a_4/a_2)[\tfrac{9}{4}(a_3/a_2)-1]+[\tfrac{27}{16}(a_3/a_2)^3+\tfrac{3}{4}(a_3/a_2)+1]\ , \qquad (6d)$$

etc. Ideally, the coefficients a_i should be obtained from a microscopic theory of the system in question, and the coefficients c_i derived from them with the help of relations (6). In practice, however, the microscopic evaluation of a_i is much too formidable as compared to the experimental determination of c_i. We, therefore, adopt a reversion of the foregoing relations and write

$$a_2=\tfrac{1}{2}mc_0^2\ , \qquad (7a)$$

$$a_3/a_2=\tfrac{2}{3}(c_1/c_0-2)\ , \qquad (7b)$$

$$a_4/a_2=\tfrac{1}{3}[c_2/c_0+\tfrac{1}{2}(c_1/c_0-3)^2]\ , \qquad (7c)$$

$$a_5/a_2=\tfrac{1}{5}\{c_3/c_0+(c_2/c_0)\ (c_1/c_0-\tfrac{8}{3})-\tfrac{2}{3}[2(c_1/c_0)^2-9(c_1/c_0)+12]\}\ , \qquad (7d)$$

etc. Hierarchy (7) enables us to derive empirically the values of the coefficients a_i *without going through a process of integration.*

By a least-squares fit of the experimental data[1,2] on $c(\rho)$ to series (5), terminated at the cubic term, we obtained the following values of c_i: For liquid He^4,

$$c_0=238.30\ \text{m/sec},\qquad c_1/c_0=2.841,\ c_2/c_0=0.096,\ c_3/c_0=-0.180, \qquad (8)$$

with a standard error of estimate 0.01 m/sec; and for liquid He^3,

$$c_0=182.90\ \text{m/sec}\ ,\qquad c_1/c_0=2.796,\ c_2/c_0=0.398,\ c_3/c_0=-0.012\ , \qquad (9)$$

with a standard error of estimate 0.02 m/sec. Relations (7) then yielded the following values of a_i: For liquid He^4,

$$a_2=13.67\ ^\circ\text{K},\quad a_3=7.66\ ^\circ\text{K},\quad a_4=0.50\ ^\circ\text{K},\quad a_5=-5.14\ ^\circ\text{K}; \qquad (10)$$

and for liquid He^3,

$$a_2=6.07\ ^\circ\text{K},\quad a_3=3.22\ ^\circ\text{K},\quad a_4=0.85\ ^\circ\text{K},\quad a_5=-1.95\ ^\circ\text{K}\ . \qquad (11)$$

The first thing one may consider here is the existence of an almost *linear* relationship between c and ρ. This was observed by Aziz *et al.*,[6] and independently by Abraham *et al.*,[2] to hold remarkably well for liquid He^4; in the case of liquid He^3, however, the latter authors observed a slight nonlinear trend as well. These features are implicit in the coefficients (8) and (9), and are directly related to the smallness of the ratio c_2/c_1. In fact, we observe that even when $(\rho-\rho_0)/\rho_0 \simeq 20\%$ the departure from linearity in the case of He^4 is less than 1%; in the case of He^3, however, the departure from linearity for a comparable value of $(\rho-\rho_0)/\rho_0$ is about 3%.

A customary way of representing this situation would be to consider a Grüneisen-like "constant" of the systems under study, viz.,

$$K\equiv\frac{\rho}{c}\left(\frac{\partial c}{\partial\rho}\right)=\frac{c_1}{c_0}+\left[2\frac{c_2}{c_0}+\frac{c_1}{c_0}\left(1-\frac{c_1}{c_0}\right)\right]\left(\frac{\rho-\rho_0}{\rho_0}\right)+\left[3\frac{c_3}{c_0}+2\frac{c_2}{c_0}-3\frac{c_2c_1}{c_0^2}-\frac{c_1^2}{c_0^2}\left(1-\frac{c_1}{c_0}\right)\right]\left(\frac{\rho-\rho_0}{\rho_0}\right)^2+\ldots\ . \qquad (12)$$

Substituting the relevant values of c_i, we obtain

$$K(\text{He}^4)=2.841-5.037\left(\frac{\rho-\rho_0}{\rho_0}\right)+13.69\left(\frac{\rho-\rho_0}{\rho_0}\right)^2+\ldots \qquad (13)$$

and

$$K(\text{He}^3)=2.796-4.225\left(\frac{\rho-\rho_0}{\rho_0}\right)+11.46\left(\frac{\rho-\rho_0}{\rho_0}\right)^2+\ldots\ . \qquad (14)$$

Clearly, the "constant" K varies considerably with ρ. To be specific, $K(\text{He}^4)$ decreases from 2.841 to 2.209 as ρ changes from 0.14513 to 0.17246 g/cm^3, while $K(\mathrm{He}^3)$ decreases from 2.796 to 1.983 as ρ changes from 0.08191 to 0.11576 g/cm^3. On the other hand, the derivative $(\partial c/\partial \rho)$ does not vary much with ρ. To see this, we introduce a parameter K^*, namely,

$$K^* \equiv \frac{\rho_0}{c_0}\left(\frac{\partial c}{\partial \rho}\right) = \frac{c_1}{c_0} + 2\frac{c_2}{c_0}\left(\frac{\rho-\rho_0}{\rho_0}\right) + 3\frac{c_3}{c_0}\left(\frac{\rho-\rho_0}{\rho_0}\right)^2 + \cdots . \tag{15}$$

The power series for K^* turn out to be

$$K^*(\mathrm{He}^4) = 2.841 + 0.192\left(\frac{\rho-\rho_0}{\rho_0}\right) - 0.540\left(\frac{\rho-\rho_0}{\rho_0}\right)^2 + \ldots \tag{16}$$

and

$$K^*(\mathrm{He}^3) = 2.796 + 0.796\left(\frac{\rho-\rho_0}{\rho_0}\right) - 0.034\left(\frac{\rho-\rho_0}{\rho_0}\right)^2 + \cdots . \tag{17}$$

Obviously, the variation of K^* is much less than that of K, which accounts for an almost *linear* dependence of c on ρ.

From a microscopic point of view, the foregoing result stems from the fact that the coefficients a_2, a_3, and a_4 (in the expansion of the ground-state energy per particle) of the given systems are such that the combination appearing on the right-hand side of (6c) is much smaller than the combination appearing on the right-hand side of (6b). It is difficult to argue from first principles why it should be so.

III. COMPARISON WITH THEORY

Theoretical calculations of the ground-state energy of liquid He^4 have been based on variational techniques employing suitable wave functions. Two examples of such a calculation are the ones by Massey and Woo[4] and by Schiff and Verlet.[5] The results of these calculations have to be corrected, in a manner suggested by Woo[7] and adopted by Roach *et al.*,[3] so that a meaningful comparison with empirical results can be effected. As demonstrated by Roach *et al.*, the theoretical results for a_2 and a_3 compare well with the ones obtained empirically. Unfortunately, the paucity of theoretical calculations prevents us from deriving reasonable values of coefficients beyond a_3.

Similar calculations for liquid He^3 have been carried out by various authors—in particular, by Woo[7] and Østgaard.[8] We have compared our empirical results with the theoretical results following from the calculations of these authors. It turns out that the theoretical value of a_2 resulting from Woo's calculations is 6.16 °K, while the value resulting from Østgaard's calculations is 6.53 °K; the empirical value obtained here is 6.07 °K. The value of a_3 resulting from Woo's calculations is about 4.5 °K, while the empirical value of this coefficient is 3.22 °K; Østgaard's calculations do not yield a reliable value for this coefficient. Again, as in the case of He^4, we are unable to make any comparisons for coefficients beyond a_3.

It is, however, possible to obtain density expansions for some of the parameters that appear in the Landau theory of Fermi liquids, as applied to liquid He^3. For instance, the ground-state sound velocity, according to this theory, is given by[9,10]

$$c^2 = \frac{p_F^2}{3mm^*}(1+F_0) = \frac{p_F^2}{3m^2}\,\frac{1+F_0}{1+\frac{1}{3}F_1}, \tag{18}$$

where m^* is the effective mass of an He^3 atom, p_F is the Fermi momentum, while F_0 and F_1 are parameters related to the Legendre transforms of the function $f(\vec{p}, \sigma; \vec{p}', \sigma')$, which appears as the second functional derivative of the total energy E of the liquid with respect to the distribution function $n(\vec{p}, \sigma)$. The parameter F_1, being directly related to m^*, can be obtained from the low-temperature specific heat of liquid He^3. Its density dependence can be extracted from the work of Anderson, Reese, and Wheatley.[11] We obtain

$$F_1 = 3[(m^*/m) - 1] = \alpha_0 + \alpha_1\left(\frac{\rho-\rho_0}{\rho_0}\right) + \alpha_2\left(\frac{\rho-\rho_0}{\rho_0}\right)^2 + \alpha_3\left(\frac{\rho-\rho_0}{\rho_0}\right)^3 + \ldots , \tag{19}$$

where $\alpha_0 = 5.6$, $\alpha_1 = 30$, $\alpha_2 = -50$, $\alpha_3 = 65$. Substituting the relevant values of p_F and m, we obtain from (18) and (19)

$$F_0 = 3.67\left(\frac{c}{c_0}\right)^2\left(\frac{m^*}{m}\right)\left(\frac{\rho}{\rho_0}\right)^{-2/3} - 1 = \beta_0 + \beta_1\left(\frac{\rho-\rho_0}{\rho_0}\right) + \beta_2\left(\frac{\rho-\rho_0}{\rho_0}\right)^2 + \beta_3\left(\frac{\rho-\rho_0}{\rho_0}\right)^3 + \ldots , \tag{20}$$

where $\beta_0 = 9.6$, $\beta_1 = 88$, $\beta_2 = 175$, $\beta_3 = -35$.

Theoretical calculation of the parameters F_1 and F_0, as a function of density, has been carried out by Tan and Feenberg.[12] Results have been reported for only three values of the particle density. Thus, a meaningful comparison can be carried out up to the linear term alone. One obtains $\alpha_0 = 3.84$, $\alpha_1 = 9.2$, $\beta_0 = 6.94$, $\beta_1 = 30$. Comparison with the empirical values of these coefficients shows that the theoretical values arising from the analysis of Tan and Feenberg are rather low. Nevertheless, the trend is in the right direction and, as already noted by these authors, approximations of uncertain magnitude in the theory call for further theoretical and numerical investigation.

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Energy Variational Principle for a Variable Number of Particles*

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Necessary and sufficient conditions are derived for the validity of the bound, $\mathrm{tr}\rho H \geqslant E_g(N_0)$, recently assumed by Abdulnur *et al.* in their paper [Phys. Rev. A **6**, 889 (1972)]. Here ρ runs over all density matrices for which $\mathrm{tr}\rho N = N_0$, the average number of electrons. H is a Hamiltonian commuting with the operator for the number of particles N, with ground-state energy $E_g(N_0)$ when the number of particles is N_0. An example is given showing that the above inequality is *not* true for every pair of commuting Hermitian operators H and N; thus this inequality differs in a fundamental way from the familiar energy variational principle. The proof of the inequality requires the property of H that the first ionization potential is greater than the electron affinity, essentially justifying the application by Abdulnur *et al.* The failure of the inequality implies that in the grand canonical ensemble there are nonzero fluctuations in N at zero temperature, with zero probability of finding $N = N_0$.

Recently a particular average energy $\langle H \rangle$ was used in a variational approach to the determination of one-electron states in central-field models for atoms.[1] Fundamental use was made of the assumption that $\langle H \rangle$ is an upper bound on the ground-state energy for a fixed average number of particles. Here, necessary and sufficient conditions for this bound to hold are derived, and the physical meaning of these conditions is discussed. A complete statement of the variational bound is

$$\langle H \rangle \equiv \mathrm{tr}\rho H \geq E_g(N_0) \qquad (1)$$

for all density operators ρ such that

$$\mathrm{tr}\rho N = N_0 \ . \qquad (2)$$

N is the operator for the number of electrons and commutes with the Hamiltonian H, $E_g(N_0)$ being the ground-state energy of H for N_0 electrons;

$$E_g(N_0) = \min_{\phi} (\phi, H\phi) \qquad \text{with } N\phi = N_0\phi \ . \qquad (3)$$

(All states are normalized to 1.)

That the correctness of the bound (1) is not general is shown by giving an example of a pair of commuting Hermitian operators H and N such that (1) is violated. Let ψ_n, $n = 1, 2, 3$, be a complete set of orthonormal vectors with $N\psi_n = n\psi_n$, $H\psi_n = E_n\psi_n$, and $\rho\psi_n = \rho_n\psi_n$. Then

$$\langle H \rangle = \sum_{n=1}^{3} \rho_n E_n \ , \qquad \mathrm{tr}\rho N = \sum_{n=1}^{3} n\rho_n \ .$$

Take $N_0 = 2$. Consistent with this and the density-operator property $\mathrm{tr}\rho = 1$ is the choice $\rho_1 = \rho_3 = \frac{1}{2}$, $\rho_2 = 0$; then

$$\langle H \rangle = \tfrac{1}{2}(E_1 + E_3) \ .$$

But clearly $E_g(2) = E_2$, and since the E_n are arbitrary, they can be chosen such that $E_2 > \frac{1}{2}(E_1 + E_3)$, violating (1). Thus it is seen that the bound (1) differs in a fundamental way from the familiar energy variational principle expressed by Eq. (3). The latter is true for any pair of commuting Her-