

THE GROUND STATE OF LIQUID ${}^4\text{He}$ IN A MODEL OF SEMI-FREE GAS

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Abstract: The expectation value of the Hamiltonian of the system of ${}^4\text{He}$ atoms is evaluated for the wave function which is the product of two-body asymptotic wave functions at small interatomic distances for each pair of particles. The corresponding integrals are performed in a similar way as in the case of hard spheres of low densities.

The liquid helium problem is formally fairly well understood. However, the numerical agreement of the theory starting from the first principles with experiment is rather poor due mainly to mathematical difficulties in treating such a problem. Improvements would be desirable for a better understanding of the whole problem. In this article we want to concentrate our attention to the ground state.

The problem of the ground state of liquid ${}^4\text{He}$ has not been analyzed so extensively as the problem of elementary excitations. Within field theoretical methods one can hardly mention any realistic approach to the solution. The well-known work of Brueckner and Sawada¹⁾ starts with the interaction potential which is infinite if the atoms are separated by a distance less than the hard sphere diameter, and is zero otherwise. Consequently there is no bound state at all. A good review of this method as well as of some others can be found in the article of Parry²⁾.

More successful achievements have been obtained within coordinate space considerations. Most of them start from the wave function³⁾:

$$\psi_n = \prod_{i < j} j(r_{ij}).$$

Wu and Feenberg⁴⁾ chose $j(r)$ in the form $\exp \frac{1}{2} u(r)$. The expectation value of the energy was written in terms of the two-particle distribution function which was determined from X-ray scattering data. Other calculations were based on this experimentally determined function. However, this approach is still not satisfactory. Quite recently Schiff and Verlet⁵⁾ have applied, within these considerations, the molecular dynamics method that had been used for classical fluids, and some time ago Mc Millan⁶⁾ used Monte Carlo computations. Although the results of these works are impressive, one would like to have a more analytical procedure.

All these works as well as the analyses of the interaction potential itself suggest an image of liquid ${}^4\text{He}$ as a gas of particles which cannot penetrate in the repulsive region of interaction. This standpoint, which we shall call a model of »semi-free

gas, is interesting for itself but also because it enables us to begin with chances for reasonable analytical successes. Such an analysis would also give some notions about correlations at large interatomic distances. In this article we apply and analyze this idea restricting ourselves to its simplest form.

We construct the trial wave function from two-particle wave functions at small interatomic distances as the product of these functions for each pair of particles. Due to special features of the asymptotic two-particle wave function at small interatomic distances we evaluate the expectation value of the ground state energy similarly to the case of hard spheres when $V \gg n \Omega_0$, where V is the volume of the system and Ω_0 the volume of a hard sphere.

1. There are several interaction potentials for helium atoms. They are all irrelevant to our method. We prefer to choose the Yntema-Schneider potential⁷⁾ because it is close to the theoretical one. The constants in this potential are not necessarily the best ones but will not be discussed here. Yntema-Schneider potential reads

$$V(r) = a e^{-\alpha r} - \frac{b}{r^6} - \frac{c}{r^8}. \quad (1)$$

The constants a , b , c , are $1200 \cdot 10^{-12}$ ergs, $1.24 \cdot 10^{-12}$ ergs, $1.89 \cdot 10^{-12}$ ergs, respectively, r is in Ångstroms, and $\alpha = 1/0.212 \text{ \AA}^{-1}$. The potential for distances of the order of atomic diameter and less is not of importance and can be ignored.

The equation of stationary states is

$$\left[\sum_i \left(-\frac{\hbar^2}{2M} \right) \Delta_i + \frac{1}{2} \sum_{i,j} V(r_{ij}) \right] \psi = E \psi. \quad (2)$$

In the limit of small interatomic distances of two particles, 1 and 2, the dominant terms in (2) are

$$\left[-\frac{\hbar^2}{2M} (\Delta_1 + \Delta_2) + a e^{-\alpha r_{12}} \right] \psi_{r_{12} \rightarrow 0} = 0. \quad (3)$$

Therefore, the asymptotic two-particle wave function at small interatomic distances is given by

$$\left(-\frac{\hbar^2}{M} \Delta + a e^{-\alpha r} \right) \varphi(r) = 0, \quad (4)$$

expressed in terms of relative coordinates.

The solution of this equation for $r \rightarrow 0$ (correctly $r \rightarrow$ atomic diameter) is

$$\varphi(r) = \text{const } e^{-Be^{-\frac{\alpha}{2}r}}, \quad (5)$$

where

$$B = \frac{2\sqrt{Ma}}{\hbar\alpha}. \quad (6)$$

By substituting (r) from (5) into (4) we obtain in the bracket

$$-\frac{\hbar^2}{M} \frac{B^2 \alpha^2}{4} e^{-\alpha r} + \frac{\hbar^2}{M} \frac{B \alpha^2}{4} e^{-\frac{\alpha}{2} r} - \frac{\hbar^2}{M} B \alpha e^{-\frac{\alpha}{2} r} \frac{1}{r} + a e^{-\alpha r}.$$

For $r \doteq 1 \text{ \AA}$ the first term is approximately 30 times larger than the other two terms.

2. The asymptotic wave function of a n -particle system at small interatomic distances is then in a model of semifree gas

$$\psi(1, 2, \dots, n) = e^{-\frac{1}{2} B \sum'_{i,j} e^{-\frac{\alpha}{2} r_{ij}}}. \quad (7)$$

Since liquid ${}^4\text{He}$ is a Bose-system, we take (7) as a trial wave function of the ground state.

3. The expectation value of the Hamiltonian of the system for the state (7) is

$$\begin{aligned} E_0 = \frac{\int \psi^* H \psi d\vec{r}_1 \dots d\vec{r}_n}{\int \psi^* \psi d\vec{r}_1 \dots d\vec{r}_n} = & \left\{ \int \psi^2 \left[-\frac{\hbar^2}{2M} \frac{B^2 \alpha^2}{4} \sum'_{i,j,j'} e^{-\frac{\alpha}{2} r_{ij} - \frac{\alpha}{2} r_{ij'}} \frac{\vec{r}_{ij} \vec{r}_{ij'}}{r_{ij} r_{ij'}} + \right. \right. \\ & + \frac{\hbar^2}{2M} \frac{B \alpha^2}{4} \sum'_{i,j} \left(1 - \frac{4}{\alpha r_{ij}} \right) e^{-\frac{\alpha}{2} r_{ij}} + \\ & \left. \left. + \frac{1}{2} \sum'_{i,j} \left(-\frac{a}{r_{ij}^6} - \frac{b}{r_{ij}^8} \right) \right] d\vec{r}_1 \dots d\vec{r}_n \right\} \left\{ \int \psi^2 d\vec{r}_1 \dots d\vec{r}_n \right\}^{-1}. \quad (8) \end{aligned}$$

Making use of the symmetry properties of the wave function and the Hamiltonian with respect to the interchange of particles we obtain

$$\begin{aligned} E_0 = & n(n-1)(n-2) \frac{\int \psi^2 \left(\frac{\hbar^2}{2M} \frac{B^2 \alpha^2}{4} \right) e^{-\frac{\alpha}{2} r_{12} - \frac{\alpha}{2} r_{13}} \frac{\vec{r}_{12} \vec{r}_{13}}{r_{12} r_{13}} d\vec{r}_1 \dots d\vec{r}_n}{\int \psi^2 d\vec{r}_1 \dots d\vec{r}_n} + \\ & + n(n-1) \frac{\int \psi^2 \left[\frac{\hbar^2}{2M} \frac{B \alpha^2}{4} \left(1 - \frac{4}{\alpha r_{12}} \right) e^{-\frac{\alpha}{2} r_{12}} - \frac{1}{2} \left(\frac{a}{r_{12}^6} + \frac{b}{r_{12}^8} \right) \right] d\vec{r}_1 \dots d\vec{r}_n}{\int \psi^2 d\vec{r}_1 \dots d\vec{r}_n}. \quad (9) \end{aligned}$$

4. The integrals in (9) are not simple. However, one may use some elaborate methods for such kind of integrals, for example the method of Ursell and Mayer and its extension. In our analysis we shall apply a simpler method, since the average interatomic distance is 4.44 \AA , the experimental value, and the effective radius of the hard-sphere of one particle determined by $\varphi(r)$, eq. (5), is 1.56 \AA . We evaluate the integrals in (9) as in the case of hard spheres when the volume of hard spheres is much less than the total volume.

The integral in the denominator is then

$$\int \psi^2 d\vec{r}_1 \dots d\vec{r}_n \doteq V (V - \Omega_0) (V - 2\Omega_0) \dots (V - (n-1)\Omega_0). \quad (10)$$

The integrals in the numerators are somewhat more complicated. Besides the ground state wave function there is one function which depends on particles 1 and 2 and one function which depends on particles 1,2 and 3. Generally speaking the value of the integrals evaluated in (10) will depend on the arrangement of integrations. In our case, however, both functions of particles 1, 2, 3 decay exponentially and the value of the integrals will be different for those integrals only, for which the integrations over particles 1, 2, 3 are performed at the beginning. Because of the large number of particles we may neglect these cases and perform the integrations over particles 1, 2, 3 at the end. The results are

$$\begin{aligned} & \int \psi^2 \Phi (1, 2, 3) d\vec{r}_1 \dots d\vec{r}_n \doteq \\ & \doteq \int \psi^2 (123) \Phi (123) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 (V - 3\Omega_0) \dots (V - (n-1)\Omega_0), \end{aligned} \quad (11)$$

$$\begin{aligned} & \int \psi^2 f (12) d\vec{r}_1 \dots d\vec{r}_n \doteq \\ & \doteq \int \psi^2 (12) f (12) d\vec{r}_1 d\vec{r}_2 (V - 2\Omega_0) \dots (V - (n-1)\Omega_0), \end{aligned} \quad (12)$$

where

$$\Phi (123) = - \frac{\hbar^2}{2M} \frac{B^2 \alpha^2}{4} e^{-\frac{\alpha}{2} r_{12}} - \frac{\alpha}{2} \frac{r_{12} \vec{r}_{12} \vec{r}_{13}}{r_{12} r_{13}} \quad (13)$$

and

$$f (12) = \frac{\hbar^2}{2M} \frac{B \alpha^2}{4} \left(1 - \frac{4}{\alpha r_{12}} \right) e^{-\frac{\alpha}{2} r_{12}} - \frac{1}{2} \frac{a}{r_{12}^3} - \frac{1}{2} \frac{b}{r_{12}^3}. \quad (14)$$

Substituting (10), (11) and (12) into (9) we obtain

$$E_0 \doteq n \frac{n-1}{V} \frac{n-2}{V-\Omega_0} I_2 + n \frac{n-1}{V} I_1, \quad (15)$$

$$I_1 = \int \psi^2 (12) f (12) d\vec{r}_1 d\vec{r}_2 \cdot \frac{1}{V-\Omega_0},$$

$$I_2 = \int \psi^2 (123) \Phi (123) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \cdot \frac{2}{V-2\Omega_0}.$$

We may neglect 1,2 and 3 with respect to n , and also Ω_0 and $2\Omega_0$ with respect to V , and write

$$\frac{E_0}{n} = I_1 \rho + I_2 \rho^2, \quad (16)$$

where $\rho = n/V$ is the density of particles.

The minimum value of E_0/n given by (16) corresponds to

$$\rho_{\min.} = - \frac{I_1}{2I_2} \quad (17)$$

and reads

$$(E_0/n)_{\min.} = - \frac{I_1^2}{4I_2}. \quad (18)$$

Inserting the values* of I_1 and I_2 in (17) and (18) we obtain

$$\rho_{\min.} = 1.30 \cdot 10^{22} \text{ cm}^{-3}, \quad (E_0/n)_{\min.} = - 2.17 \cdot 10^{-16} \text{ ergs.} \quad (19)$$

while the experimental values are

$$\rho_{\text{exp.}} = 2.19 \cdot 10^{22} \text{ cm}^{-3}, \quad (E_0/n)_{\text{exp.}} = - 9.73 \cdot 10^{-16} \text{ ergs.} \quad (20)$$

5. The agreement with experiment is rather poor although the evaluated energy is negative and the density is not too far from the experimental value. We conclude that one particle must be kept by another particle more strongly in the region of the attractive part of the potential, which should be expressed in the wave function. Some improvement can also be achieved with a better correlative function at small interatomic distances but without greater changes because of the small radius of »rigidity« of a particle in comparison with the average interatomic distance.

Now, let us consider the fulfilment of the condition $V \gg n \Omega$ for $\rho_{\min.}$. According to (19)

$$n = 1.30 \cdot 10^{22} V.$$

The equation for Ω_0 is

$$\int (1 - \psi^2(r)) d\vec{r} = 8 \Omega_0.$$

After evaluating the left side one obtains

$$\Omega_0 = 16.02 \cdot 10^{-24} \text{ cm}^3.$$

The ratio $V/(n\Omega_0)$ is then 4.81. This ratio is not quite satisfactory but it shows that better evaluations of the integrals will not essentially change the results. For $\rho \rightarrow 0$ the condition $V \gg n\Omega_0$ can be arbitrarily satisfied, the bound state being still contained in it.

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* The numerical evaluation of the I_1 and I_2 were performed at the Numerical Centre of the Institute for metallurgical investigations in Zenica.

OSNOVNO STANJE TEKUĆEG ${}^4\text{He}$ U MODELU POLUSLOBODNOG
PLINA

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S a d r Ź a j

Tekući ${}^4\text{He}$ razmatran je kao sistem čestica koje ne mogu prodrijeti u područje odbojnog dijela međudjelovanja a u preostalom dijelu prostora se ponašaju slobodno.

Pokusna valna funkcija (7) konstruirana je uzimanjem produkta dvočestičnih asimptotskih valnih funkcija za male međučestične udaljenosti (5). Očekivana vrijednost energije proračunata je za ovu valnu funkciju u aproksimaciji »čvrstih kugli«. Dobivena je kvadratična zavisnost energije o gustoći (16). Zatim je nađena minimalna vrijednost energije (18) i odgovarajuća gustoća (17) i to je uspoređeno sa eksperimentalnim podacima. Nije postignuto zadovoljavajuće slaganje ali je pokazano da je model »poluslobodnog plina« dobra osnova za izgradnju teorije tekućeg ${}^4\text{He}$.