COMMENTS ON THE THEORY OF EVAPORATION FROM SUPERFLUID He^4

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The revised theory of evaporation from superfluid helium based on the Bogoliubov model of interacting many-boson systems is presented. In contrast to previous theoretical calculations no sizable shift towards higher energies of the energy distribution function for evaporated atoms is obtained. Our results are in much better agreement with the revised version of the original King and Johnston experiment which indicated no shift in the energy of the evaporated atoms. Using our model we are able to trace the assumptions that have led in the previous theories to the prediction of a shift.

1. Introduction

Some preliminary experimental results obtained by King and Johnston [1] caused a growing interest in the theory of evaporation from superfluid helium.

The experiment reported in [1] seems to indicate that the energy distribution function of evaporated atoms is shifted towards higher energies, by approximately 1.1°K, in the investigated range of temperatures of the liquid. This experiment, which was essentially based on the atomic beam technique, was quite involved and subsequent and more careful and selective measurements [2] performed with the use of a different experimental technique [2b] showed that there is no shift towards higher energies, at least within the experimental accuracy. Since the publication of [1] several theoretical papers appeared in the literature, all of them predicting the existence of the unobserved shift. The most thorough analysis of the evaporation from He II published so far is that of Hyman et al., [3] and is based on the use of the tunneling hamiltonian technique. This work however belongs to the category of shift predicting theories.

In several papers the tunneling hamiltonian technique was used for the description of the interactions between two Bose systems. For example, it was used for the construction

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of a theory of the Kapitza resistance [4], and, in a previous paper by one of us, for an account of the Josephson effect between two Bose systems [5]. In the present paper we make an attempt to resolve the theoretical puzzle and to show that the tunneling hamiltonian technique, properly handled, gives an answer that is in better agreement with the experimental situation. Because the microscopic theory of He II is far from being simple, we decide for our purposes upon a very simplified model of an interacting Bose system, namely, the Bogoliubov model. This model is not quantitatively good for liquid He II, but all the fundamental properties of superfluidity can be understood on the basis of its properties. Thus we believe that the enormous shift in the energies (1.1°C when the temperature of the liquid is 0.6°C) — if real — should also be understandable on the basis of the Bogoliubov model. The essential ingredient of this model is the spectrum of elementary excitations of the liquid. As it was anticipated that the origin of the shift is due to the infinite density of states for rotons, we decide to use the Bogoliubov model with a “realistic” interatomic potential. Realistic here means that the spectrum of bogolons has the characteristic shape of the Landau excitations curve, that is, with the high energy phonon maximum and the roton minimum.

The plan of this paper is as follows. In Section 2 we formulate the tunneling hamiltonian approach and we discuss in some detail the parameters that enter into the hamiltonian. In Section 3 we sketch the very elementary calculations which allow us to express the total rate of evaporation from the liquid in terms of an integral of the spectral function. In Section 4 we discuss the results obtained by the explicit computation of the rate calculated in Section 3. From these results one can easily see that the infinite density of states associated with the roton minimum and the high energy phonon maximum has no effect whatsoever on the rate of evaporation, since the peaks associated with these two singular points of the excitation curve occur in the tail of the Bose-Einstein distribution function. Section 5 is devoted to conclusions and to some speculations about a more correct treatment of the evaporation effect.

2. Formulation of the model

The experimental situation in the King and Johnston apparatus was the following. The liquid helium at a temperature of $T = 0.6°C$ was contained in a closed cell from which the liquid vapor was pumped. Due to the well known properties of helium one can achieve in the cell and exhaust tube a vacuum of the order of $10^{-5}$ atm. In the completely different experiment reported in Ref. [2b] the mean free path of the helium atoms in the vapor at $T = 0.6°C$ was estimated to be 2 mm. These facts allow us to treat the gas of helium atoms above the liquid as a gas of free particles. As the pumping was sustained during the experiment the helium gas of evaporated atoms was not in thermodynamic equilibrium with the liquid. Using the grand canonical equation of state, one can easily prove that, at such experimental conditions, the chemical potential in the vapor is equal to zero. This allows us to write the hamiltonian of the vapor as:

$$ H_v = \sum_p \varepsilon_p a_p^\dagger a_p, $$

(2.1)
where $a_p$ and $a_p^+$ are annihilation and creation operators, respectively, for helium atoms with momentum $p$, and $e_p$ is the free particle energy $e_p = p^2/2m$.

We assume that liquid helium at $T = 0.6^\circ K$ can be described, in a fairly crude way, by means of the Bogoliubov model. However, in order to keep some contact with reality, we also assume that the interparticle potential is chosen in such a way that the bogolon spectrum satisfies two conditions: (1) in the small momenta limit the slope of the energy versus momentum curve gives the correct velocity of sound at $T = 0.6^\circ K$; (2) the spectrum has the roton minimum. These two conditions can be satisfied by the so-called realistic potentials. Here we have chosen the delta-shell potential, whose Fourier transform has the form

$$V(p) = V_0 \frac{\sin(p\sigma)}{p\sigma}. \quad (2.2)$$

In (2.2) the parameter $V_0$ is related to the velocity of sound $c$ via the formula $n_0 V_0 = mc^2$, where $n_0$ is the condensate density and $m$ is the mass of the He$^4$ atoms. The parameter $\sigma$ is related to the scattering length and in our calculations was set equal to 2.5 Å.

The Bogoliubov Hamiltonian has the form [8]:

$$H_F = \sum_p (e_p - \mu)b_p^+b_p + \frac{1}{2} n_0 \sum_p V(p) \left( b_p^+b_p + b_p^+b_{-p} + b_{-p}^+b_{-p} + b_{-p}^+b_{-p} \right), \quad (2.3)$$

where $V(p)$ is given by (2.2) and $n_0$ is the condensate density. By using standard diagonalization procedures one can derive from (2.3) the bogolon excitation spectrum $E_p$:

$$E_p = \{e_p^2 + 2 n_0 V(p) e_p \}^{1/2}. \quad (2.4)$$

For completeness we shall write down the expression for the parameters $u_p$ and $v_p$ which appear in the Bogoliubov transformation:

$$u_p^2 = 1 + v_p^2 = \frac{1}{2} \left( -1 + (e_p + n_0 V(p)) / E_p \right). \quad (2.5)$$

Having established the form of the Hamiltonian for two separate interacting systems, we can follow the scheme of the standard tunneling technique and write the interaction term in the following way:

$$H_{\text{int}} = \sum_{p_1, p_2} T_{p_1, p_2} (a_{p_1}^+ a_{p_2} + a_{p_2}^+ a_{p_1}). \quad (2.6)$$

The first term in the equation (2.6) describes the annihilation of one atom with momentum $p_2$ in the liquid and the creation of one "vapor" atom with momentum $p_1$. The second term describes the inverse process, and the transition probability is given by $T_{p_1, p_2}$. The full Hamiltonian of this system is:

$$H = H_V + H_F + H_{\text{int}}. \quad (2.7)$$

Note that in the limit $T_{p_1, p_2} \to 0$ we obtain the Hamiltonian in the form of a sum of two independent systems. This is the fundamental assumption in the tunneling Hamiltonian approximation. The details of the "evaporation", that is, of the jumping of one of the atoms from the liquid into the vapor, are hidden in the matrix $T_{p_1, p_2}$. 


3. Rate of evaporation

The probability of evaporation of an atom from the liquid into the vapor is given, according to the Fermi "golden rule", by the following expression:

\[ \mathcal{W}_{i \rightarrow f}(p, n_p) = \frac{2\pi}{\hbar} |\langle n_p + 1, f | H_{\text{int}} | n_p, i \rangle|^2 \delta(E_f - E_i + \varepsilon_p), \tag{3.1} \]

where the state \( |n_p, i\rangle \) is the initial state of the combined system, with \( n_p \) particles (with momentum \( p \)) in the vapor and the liquid in the state \( |i\rangle \). \( |n_p + 1, f\rangle \) is the final state with one additional particle in the vapor and the liquid in the final state \( |f\rangle \). \( E_f \) and \( E_i \) are the final and initial liquid energies respectively.

The substitution of \( H_{\text{int}} \) given by (2.4), into (3.1) leads to the equation

\[ \mathcal{W}_{i \rightarrow f}(p, n_p) = \frac{2\pi}{\hbar} \delta(E_f - E_i + \varepsilon_p) \langle n_p + 1 \rangle \sum_{p_1, p_2} T_{p_1, p} T_{p_2, p} \langle f | b_{p_1}^\dagger | i \rangle \langle i | b_{p_2}^\dagger | f \rangle. \tag{3.2} \]

The total rate of evaporation should then be given as the thermal average of (3.2):

\[ R(p, n_p) = \sum_{i, f} P_i \mathcal{W}_{i \rightarrow f}(p, n_p). \tag{3.3} \]

where \( P_i \) is the Boltzmann factor of the initial state.

Using the properties of the \( b_p \) operators in the Heisenberg representation we can rewrite (3.3) as:

\[ R(p, n_p) = \frac{2\pi}{\hbar} (n_p + 1) \sum_{p_1, p_2} T_{p_1, p} T_{p_2, p} \int \frac{dt}{2\pi\hbar} e^{i\varepsilon_p \omega t} \langle b^+_p(0) b_p(t) \rangle, \tag{3.4} \]

where \( \langle \ldots \rangle \) denotes a thermal average. The quantity \( \langle b^+_p(0) b_p(t) \rangle \) appearing in (3.4) is one of the correlation functions introduced in [6] namely:

\[ G^<(p, t; p', t') = -i \langle b^+_p(t') b_p(t) \rangle. \tag{3.5} \]

Going to the Fourier space one can easily find the following relation between \( G^< \) and the spectral function \( A(p, z) \):

\[ G^<(p, z) = f_B(z) A(p, z), \tag{3.6} \]

where \( f_B(z) \) is the Bose-Einstein distribution. Using (3.6) we can rewrite (3.4) as follows:

\[ R(p, n_p) = \hbar^{-2}(n_p + 1)f_B(\varepsilon_p) \sum_{p_1, p_2} T_{p_1, p} T_{p_1 + p_2, p} A(p, \varepsilon_p), \tag{3.7} \]

and denoting

\[ \sum_{p_1} T_{p_1, p} T_{p_1 + p_2, p} = M(p_2, p), \]

it comes:

\[ R(p, n_p) = \hbar^{-2}(n_p + 1)f_B(\varepsilon_p) \sum_{p_2} M(p_2, p) A(p_2, \varepsilon_p). \tag{3.8} \]
Under the experimental conditions described in reference [1] we are interested only in the rate \( R \) in which the initial vapor states are not occupied, that is, \( n_p = 0 \). We are also going to make a rather unrealistic assumption concerning the coefficients \( M(p_2, p) \), that is, \( M(p_2, p) = M = \text{constant} \).

Although this assumption is made in all the tunneling calculations it is an evident oversimplification. Indeed, the matrix elements \( T_{p_1, p_2} \) and, of course, \( M \) depend very strongly on the momenta of the particles. However, very little is known so far about the microscopic theory of transition of a single atom through the liquid helium-vacuum interface. The calculation of \( T_{p_1, p_2} \) becomes rather involved because one has to take into account the scattering of atoms from the surface excitations, the diffuse character of the interface, etc. As one lacks any reasonable knowledge of the momentum behaviour of \( T_{p_1, p_2} \), the assumption \( M = \text{constant} \) seems adequate at the present time; the consequences of this assumption will be discussed in Section 5.

Taking into account the simplifications introduced in the last paragraph, the equation (3.8) for the rate becomes:

\[
R = \hbar^{-2} M f_p(e_p) \sum_{p'} A(p', e_p). \tag{3.9}
\]

This expression is the fundamental formula in our calculations. In order to see that (3.9) is really the correct expression, let us check the result one obtains in the limit, where the liquid is treated as a gas of free particles. \( A(p, x) \) is then given by

\[
A(p', e_p) = 2\pi \delta(e_p - p'^2/2m). \tag{3.10}
\]

The summation in (3.9) may be changed into an integral, and we have

\[
R = \frac{\Omega}{\pi \hbar^2} M M f_p(e_p) |p|. \tag{3.11}
\]

The quantity that is directly measurable is the rate of emission \( \tilde{R} \), into an energy interval \( de_p \) around \( e_p \). So we have:

\[
\tilde{R} = (\text{const})e_p f_p(e_p), \tag{3.12}
\]

which is in agreement with the result obtained on the basis of elementary physical considerations. In the next sections we shall compute the rate \( \tilde{R} \) for the Bogoliubov system.

4. Theoretical computations

The Green functions and the spectral function \( A(p', e_p) \) can be easily computed for the system of Bose particles described by the Bogoliubov model. The spectral function is given by [8]

\[
A(p, e) = 2\pi v_p^2 \delta(e - E_p) - 2\pi v_p^2 \delta(e + E_p), \tag{4.1}
\]

where \( u_p \) and \( v_p \) are given by equation (2.5) and \( E_p \) is the bogolon excitation energy given by (2.4). It should be noted that the spectral function (4.1) corresponds to the lowest
order approximation in the Bogoliubov theory, that is, to the case of noninteracting bogolons. It is feasible to go to higher order and to include interactions between bogolons, but we shall not do so in the present paper.

Substituting (4.1) into (3.9) we can observe that the second term in (4.1) contributes nothing to \( \hat{R} \). Changing the sum over momenta into an integration, and using well known properties of delta functions, we can write:

\[
\hat{R} = (\text{const}) \sqrt{\varepsilon f_p(\varepsilon)} \sum_{p_0} \left\{ p^2 \mu_p \left| \frac{dE_p}{dp} \right|^{-1} \right\}_{p=p_0},
\]

(4.2)

where \( p_0 \) is a root of the equation \( \varepsilon = E_p \).

Expression (4.2) is our final result. Using the energy spectrum given by (2.4), computed for the delta-shell potential (see Fig. 1), we performed numerical calculations of (4.2) for energies \( \varepsilon \) from 0 to \( 12^\circ\)K. The results are presented in Fig. 2. From Fig. 1 it is clear

![Fig. 1. Energy spectrum for the Bogoliubov model (Eq. (2.4)) assuming a delta-shell potential (Eq. (2.2)), with \( n_0 V_0 = mc^2 = 27.06^\circ\)K and \( \sigma = 2.5\) Å.](image)

that our excitation energy curve is in good agreement with the measured velocity of sound at \( T = 0.6^\circ\)K. The roton minimum is shifted towards the low momenta region by \( 0.5\)Å\(^{-1}\), but this is not important for the interpretation of our results. Fig. 2 shows the rate plotted as a function of energy (solid line); the dashed lines represent the free particle rate given by (3.12).

As it is evident from the curve in Fig. 2, the maximum of the rate is shifted for the Bogoliubov system by about \( 0.35^\circ\)K. The shape of the curve is indeed Maxwellian and the two peaks due to the infinite density of states \( (dE_p/dp = 0) \) associated with the roton minimum and the high energy phonon maximum (see Figure, 1) appear in the tail of the distribution function and are completely suppressed.
The small shift in the rate is quite stable and independent of the details of the potential that we are using. The same form of rate is obtained if instead of using the delta-shell potential we use the \( \delta(r) \) potential. In this case the roton minimum disappears from the excitation curve (Fig. 1), but the rate remains virtually the same. Of course, the peaks A and B are then no longer present. As we see, the shift towards higher energies which is obtained from this calculation is much smaller than the one reported by King and Johnston. Furthermore, our curve is geometrically analogous to a Maxwellian, in contrast to the curves obtained in previous calculations. Since the more recent experiments indicate that there is no shift whatsoever, we should now try to find the proper explanation for the fact that we obtained a small, but by no means negligible, shift.

We feel that there are two essential reasons why our model still predicts a small shift. First, the assumption that \( T_{p1,p2} \) is constant certainly lacks a good deal of realism. There seems to be little doubt that the low energy atoms should not have too much influence on the rate of evaporation. Therefore \( T_{p1,p2} \) for small values of the momenta should be much smaller than for higher values. Any change of the matrix \( T \) must have serious consequences in the form of \( \tilde{R} \), and we feel that the shift may be suppressed by a more realistic choice of \( T_{p1,p2} \).

On the other hand our model may be modified a little along the line proposed by Anderson [7]. From an analytical point of view Anderson's argument means that the \( \varepsilon \) in the equation for the rate, being the energy of the evaporated atoms, should be counted not from zero but from some threshold energy \( \eta \). Anderson assumed that \( \eta \) should be equal to the negative value of the chemical potential in the liquid, that is, \( \eta = 7.15^\circ \text{K} \). When this
is assumed in our calculations the solid curve in Fig. 2 changes drastically and one obtains the form shown schematically in Fig. 3.

The phonons now are completely unimportant, the rotons dominate the emission, and we actually have the maximum around 1.7°K, that is, in the vicinity of the maximum observed in [1]. The curve in Fig. 3 has however little in common with either a Maxwellian or a Bose-Einstein distribution function.

The result in Fig. 3 was obtained by assuming that the work function for the liquid should be identical to the chemical potential \( \mu \). There seems to be no justification for this assumption. It is certainly true that there must be some threshold energy, and indeed by assuming \( \eta = 0.3°K \) we are able to obtain a rate which has its maximum at 0.6°K, in agreement with the observable situation. In this case peaks A and B are still well in the tail of the distribution function and therefore are completely negligible.

5. Conclusions

In the last section we described the results that follow from the particular model chosen for the liquid system. The liquid was assumed to described by means of the Bogoliubov model and the vapor was considered as a gas of free particles. Our results seem to be in much better agreement with experiment than those published previously.

We also indicated the presence of at least two effects that can certainly contribute to any shift of the maximum of the evaporation rate. However, we believe that such effects are essentially due to the surface. For example, the free surface of superfluid helium supports elementary excitations in the form of ripples, which are not included in our calculations.
The very existence of the surface will modify our assumption of translational symmetry for the matrix $T_{\rho_1,\rho_2}$, and will produce a much more complicated spectral function $A$. In conclusion, we performed the calculation of the rate of evaporation of atoms from superfluid helium using the tunneling hamiltonian technique and assuming the Bogoliubov model for the superfluid. No surface effects were included and all the conventional simplifications of the tunneling were used.

Using the realistic form of the bogolon excitation spectrum we were able to prove that the emission due to the rotons and to the high energy phonons is unimportant. The theoretical curve is similar to a Maxwellian distribution function, but its maximum is slightly shifted towards the high energy side by approximately $0.35^\circ K$. This shift is much smaller than predicted by previous theoretical calculations, but might be easily measured experimentally. Because the improved experiments [2b] indicate that there is no shift of the maximum, we discuss two conjectures for this peculiar result of our model. The first one is based on a critical examination of the tunneling approximation itself, and the second assumes Anderson's suggestion that there must be a work function associated with the evaporation process. The value of the work function which is needed to bring our theoretical results to a good agreement with experiment is about $0.3^\circ K$. This will produce a Maxwellian rate with its maximum at $T = 0.6^\circ K$, the same temperature of the superfluid liquid. Such a value is again in contradiction with the older theories which assumed that the work function should be equal to the negative of the chemical potential of the liquid, that is, $\eta = 7.15^\circ K$. This high value of $\eta$ yields the evaporation curve shown in Fig. 3, which has its maximum shifted by $1.15^\circ K$ from the temperature $T = 0.6^\circ K$ of the liquid, and which looks very different from a Maxwellian.

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