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QUANTITATIVE ANALYSIS OF THE URSELL-MAYER METHOD AND SEMI-FREE GAS MODEL IN THE THEORY OF LIQUID HELIUM*

A. BULJAN-JADRIĆ and S. KILIĆ**

Department of Electrical Engineering University of Split, Split

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Abstract: In this paper we show that the Ursell-Mayer method is unpractical in the theory of liquid helium. The model of »semi-free gas« gives a good qualitative result for the ground state energy and is correct in the zero density limit; a plausible above limit range of densities of its applicability is derived here.

1. Introduction

The systems of many identical particles, which interact through a two body potential, strongly repulsive at a short range and attractive at a long range, have been intensively investigated in the past twenty years. The Bijl-Jastrow method[1] has been succesful in describing such systems. For a boson system of N identical particles confined to a volume Ω, with Hamiltonian

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}\Delta_i + \frac{1}{2}\sum_{i,j} V(r_{ij}) \tag{1}$$

trial wave function has the form

$$\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \prod_{1\leqslant i<j\leqslant N} f(r_{ij}), \tag{2}$$

where $f(r_{ij})$ is a function of the distance between particles i and j.

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** Department of Civil Enginnering of Split

Wu and Feenberg[2] chose

$$f(r_{ij}) = e^{\frac{1}{2} u(r_{ij})} \tag{3}$$

with

$$u(r_{ij}) = u({}_{ij}) = -\left(\frac{a_1}{r}\right)^{a_2}; \tag{4}$$

a_1 and a_2 are variational parameters. This form of the function f presents a parameterized solution of the two body problem at small interatomic distances and has been used in later papers[3,4].

The model of semi-free gas was formulated in 1968. and has been especially applied[5] to liquid ^{4}He. It has been shown that this model describes exactly the systems when the density of particles goes to zero. As almost all other papers on this subject, Ref.[5] contains as the main difficulty the solution of multi-dimensional integrals. Some numerical methods, as the Monte Carlo and molecular dynamics procedure, have been applied to the determination of these integrals [3,4]. Also several analytic methods have been developed, for instance[6,7] and these integrals have been found as a formal expansion with respect to density. The coefficients in this expansion are integrals of lower dimensionality.

In this paper we report the results of a numerical calculation of the ground state energy in the approximation of the second order of the Ursell-Mayer expansion[7]. By using the correlation function $u(ij)$ from the paper of Shiff and Verlet[4]

$$u(r) = -\left(\frac{\sigma b}{r}\right)^5 \tag{5}$$

and the Lennard-Jones potential

$$V(r) = 4\,\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{6}$$

where

$$b = 1.16,$$
$$\sigma = 2.556\ \text{Å},$$
$$\varepsilon = 10.22\ \text{K},$$

we can obtain several useful conclusions. It is shown here that the Ursell-Mayer (as well as the Iwamoto and Yamada) method is not practical in the theory of quantum fluids. It is found also that model semi-free gas of liquid ^{4}He can be used if dentisities are at least about ten times less than real density of liquid ^{4}He.

Let us mention that $u(r_{ij})$ also depends on the distribution of other particles, that is, $u(r_{ij})$ is function of the density too. This connection is given, for example, by the Bogoliubov-Born-Green-Kirkwood exact formula, or by two approximative formulas »hypernetted chain« and Percus-Yevick[8]. Since the solutions of these equations are not known, we used the same form (5) for real and lower densities. It means that our result for the model of semi-free gas is referred in the context of this approximation.

2. *Application of Ursell-Mayer method*

The ground state energy of a boson system for wave function (2) and (3) is

$$\frac{E}{N} = \varrho \frac{1}{\Omega} \int e^{u(12)} F_2(12)\, G_2(12)\, d\vec{r}_1\, d\vec{r}_2 + \varrho^2 \frac{1}{\Omega} \int e^{u(12)+u(13)+u(23)} F_3(123)\, G_3(123)\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3, \tag{7}$$

where

$$F_2(12) = \frac{1}{2} V(r_{12}) - \frac{\hbar^2}{4m} \Delta_1 u(r_{12}) - \frac{\hbar^2}{8m} \nabla_1 u(r_{12})\, \nabla_1 u(r_{12}), \tag{8}$$

$$F_3(123) = -\frac{\hbar^2}{8m} \nabla_1 u(r_{12})\, \nabla_1 u(r_{13}), \tag{9}$$

$$G_2(12) = \Omega^2 e^{-u(12)} \frac{\int \underset{e^{ij}}{\sum} u(ij)\, d\vec{r}_3\, d\vec{r}_4 \dots d\vec{r}_N}{\int \underset{e^{ij}}{\sum} u(ij)\, d\vec{r}_1\, d\vec{r}_2 \dots d\vec{r}_N}. \tag{11}$$

The functions G_2 and G_3 can be written as a series with respect to the density[7]

$$G_2 = 1 + \varrho\, [g(12) - \alpha] + \varrho^2 \left[\alpha^2 - \frac{1}{2} \beta - \alpha g(12) + \frac{1}{2} h(12)\right] + \dots, \tag{12}$$

$$G_3 = 1 + \varrho\, [p(123) - \lambda] + \dots, \tag{13}$$

where

$$g(12) = \int (e^{u(13)+u(23)} - 1)\, d\vec{r}_3, \tag{14}$$

$$h(12) = \int (e^{u(13)+u(23)} - 1)(e^{u(14)+u(24)} - 1)\, d\vec{r}_3\, d\vec{r}_4, \tag{15}$$

$$p(123) = \int (e^{u(14)+u(24)+u(34)} - 1)\, d\vec{r}_4, \tag{16}$$

$$\alpha = \frac{1}{\Omega} \int e^{u(12)} (e^{u(13)+u(23)} - 1)\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3, \tag{17}$$

$$\beta = \frac{1}{\Omega^2} \int e^{u(12)} (e^{u(13)+u(23)} - 1)(e^{u(14)+u(24)} - 1) \cdot$$

$$\cdot\, e^{u(34)}\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4, \tag{18}$$

and

$$\lambda = \frac{1}{\Omega^3} \int e^{u(12)+u(13)+u(23)} (e^{u(14)+u(24)+u(34)} - 1) \cdot$$

$$\cdot\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4. \tag{19}$$

Now the equation (7) gets the following form

$$\frac{E}{N} = \varrho\, I_1 + \varrho^2 (I_{21} + I_{22} + I_{23}) + \varrho^3 (I_{31} + I_{32} + I_{33} + I_{34} + I_{35}), \tag{20}$$

with

$$I_1 = \frac{1}{\Omega} \int e^{u(12)} F_2(12)\, d\vec{r}_1\, d\vec{r}_2, \tag{21}$$

$$I_{21} = \frac{1}{\Omega} \int e^{u(12)} F_2(12) (e^{u(13)+u(23)} - 1)\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3, \tag{22}$$

$$I_{22} = \frac{1}{\Omega} \int e^{u(12)+u(13)+u(23)} F_3(123)\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3, \tag{23}$$

$$I_{23} = -\alpha\, I_1, \tag{24}$$

$$I_{31} = \frac{1}{2\Omega} \int e^{u(12)} F_2(12) (e^{u(13)+u(23)} - 1)(e^{u(14)+u(24)} - 1) \cdot$$

$$\cdot\, e^{u(34)}\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4, \tag{25}$$

$$I_{32} = \frac{1}{\Omega} \int e^{u(12)+u(13)+u(23)} F_3(123) (e^{u(14)+u(24)+u(34)} - 1) \cdot$$

$$\cdot\, d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4, \tag{26}$$

$$I_{33} = -\alpha\, I_{21}, \tag{27}$$

$$I_{34} = (\alpha^2 - \frac{1}{2}\beta)\, I_1, \tag{28}$$

$$I_{35} = -\lambda \cdot I_{22}. \tag{29}$$

These integrals have been evaluated numerically; their values are

$$I_1 = -(4.766 \pm 0.005) \cdot 10^{-38},$$
$$I_{21} = (2.12 \pm 0,02) \cdot 10^{-59},$$
$$I_{22} = (6.06 \pm 0.07) \cdot 10^{-61},$$
$$I_{23} = -(2.307 \pm 0.005) \cdot 10^{-59},$$
$$I_{31} = -(0.46 \pm 0.08) \cdot 10^{-80},$$
$$I_{32} = -(0.38 \pm 0.08) \cdot 10^{-81},$$
$$I_{33} = (1.03 \pm 0,02) \cdot 10^{-80},$$
$$I_{34} = -(0.559 \pm 0.005) \cdot 10^{-80},$$
$$I_{35} = (0.4406 \pm 0.0005) \cdot 10^{-81}.$$

If $\varrho = \varrho_0 \cdot 10^{22}$ is substituted and if the values of the integrals are inserted, we find

$$10^{16} \cdot \frac{E}{N} = -4.766\,\varrho_0 - 1.3\,\varrho_0^2 + a\,\varrho_0^3. \qquad (30)$$

The problems which have arisen during numerical integration refer mainly to the integrals I_{21}, I_{31} and I_{32}. The integral I_{21} can be reduced to a triple integral and calculated by means of Simpson's formula. The relative error of 10^{-2} could be attained with about four hours operation of a big computer. There was sense in calculating the integrals I_{31} and I_{32} by applying the Monte Carlo method, as they cannot be reduced to lower than sevenfold ones. The results of the applied Monte Carlo procedure depend considerably on the choice of initial numbers, so the accuracy of the evaluation of these integrals is from 10 to 16%. In the relation (30) the coefficient of ϱ_0^2 has absolute error ± 0.2. The absolute value of the coefficient a is not larger than 10; although this coeficient has been calculated with a larger error, we can use the relation (30) for profitable analysis.

3. Discussion

The first term in (30) cannot in principle describe energy as function of density, because for the real densities its value is below the experimental one. The first two terms together make this situation still worse, the energy becomes still smaller and for experimental density considerably exceeds the experimental value of $-9.86 \cdot 10^{-16}$ erg/particle. If we suppose that the third term follows the monotony of the series, it equals approximately »+« or »—« 0.35. If we expect a fast convergence of the series, we can suppose that the third term is positive (otherwise everything will be still worse) and again for experimental density the energy $-12.8 \cdot 10^{-16}$ erg/particle is attained. All this suggests that it is neccesary to add further terms of the series[9], whereby we are actually returned to the initial problem, since multiplicity of the integrals increases with the power of the density. So e. g. with the first power of density there comes necessarily at least an integral over one variable, with the second power an integral over three variables and with the third power an integral over seven variables. This shows that the Ursell-Mayer method in this form is suitable only for qualitative analysis, while it is quite unpractical for real densities. Since the results from[3,4] for the ground state energy are close to the experimental values, it can be established further that a possible improvement of the Wu-Feenberg type trial wave function[10–14] will not change this conclusion in any considerable degree.

The integral I_1 in Ref.[5] has been calculated for the Yntema-Schneider potential and non-parameterized two-particle function (3) with result $-3.73 \cdot 10^{-38}$. This value is close to $-4.766 \cdot 10^{-38}$ which has been found here for the Lennard-Jones 12—6 potential and for the best parameterized wave function (3). The value of energy increases when the parameterized wave function assumes the form of the non-parameterized one[5], which means that the values of the integral I_1 are still closer. This then shows an almost negligible influence of the choice of potentials, which are available for the helium atoms, on the results.

The first term in the relation (30) is ten times larger than the second one, if the density is equal to $0.36 \cdot 10^{22}\,\mathrm{cm}^{-3}$. This value can be considered as a limit below which just the first term of the energy series is a relatively good approximation. With this the quantitative meaning of the term »density goes to zero« in the semi-free gas model of liquid helium is defined at the same time[5].

It would have been worth while if the results in Refs.[3,4] had been found for the densities for which the first term of the Ursell-Mayer expansion is good approximation. In this way a possibility of checking the correctness of the numerical methods used in these papers would be obtained. The mentioned error of 2% seems to be a bit too good when comparing it with those from our experience.

Let us mention at the end that the numerical calculations have been performed at the Split Terminal of the Zagreb University computing Centre.

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KVANTITATIVNA ANALIZA URSELL-MAYEROVOG POSTUPKA I MODELA POLUSLOBODNOG PLINA U TEORIJI TEKUĆEG HELIJA

A. BULJAN–JADRIĆ i S. KILIĆ

Elektrotehnički fakultet, Split

Sadržaj

Energija osnovnog stanja tekućeg ^{4}He predočena je sa prva tri člana Ursell-Mayerovog razvoja i proračunata. Optimizirana dvocestična valna funkcija Wu, Feenberg i Ljoljina tipa uzeta je iz Shiff i Verletova rada$^{4)}$.

Račun pokazuje da prvi član u razvoju daje energiju koja je znatno niža od eksperimentalne. Drugi član ovu situaciju još više pogoršava. Iako je treći član proračunat sa znatnim odstupanjem, zaključeno je da Ursell-Mayerov postupak nije primjenljiv u teoriji tekućeg helija.

Utvrđena je također granica gustoće, za koje je prvi član u Ursell-Mayerovom razvoju dominantan. Ovim je izvedeno područje primjenljivosti modela poluslobodnog plina. Pokazano je da se model poluslobodnog plina može upotrijebiti ako se uzmu gustoće iz područja čija je gornja granica približno deset puta manja od eksperimentalne.

Polazeći od činjenica da je Shiff i Verletov rezultat vrlo blizu eksperimentalnom, utvrđeno je nadalje da eventualno poboljšanje valne funkcije neće promijeniti taj zaključak.