Ground-state properties of two-dimensional liquid and solid ⁴He[†]

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Variational calculations of two-dimensional liquid and solid states of ⁴He interacting by a Lennard-Jones potential are presented. The lowest-energy state of this system at $T = 0$ is shown to be the liquid phase. At higher densities, the system does crystallize. The melting and solidification densities are computed; the melting behavior is compared with the observed melting of solids in two dimensions. The errors of previous approximate calculations are discussed.

I. INTRODUCTION

It is well known[1] that at $T = 0$ the lowest-energy state of ⁴He is a liquid state, and it only crystallizes at higher densities under external pressure. This fact is attributed to the large zero-point motion of ⁴He atoms. Since the degree of importance of zero-point motion may depend on the dimensionality of the system, it is interesting to investigate whether a two-dimensional Bose system with similar interaction would behave in the corresponding way. In this paper, results of such an investigation are reported.

In previous calculations on the two-dimensional liquid phase of a Bose system in which particles interact with a Lennard-Jones potential, both a Monte Carlo method[2] and the molecular-dynamics[3] method were employed to compute the variational energy in the low-density region ($\rho\sigma^2 < 0.33$). Several approximate integral equations [Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY), Percus-Yevick, and hypernetted chain] were used to extend the liquid-phase calculations to a higher density range[4] ($\rho\sigma^2 \leqslant 0.46$). However, it is well known from the classical theory of liquids[5] that these approximations are not accurate in the high-density region, especially near melting. It is also clear from Ref. 4 that the BBGKY integral equation leads to errors at quite low densities ($n\sigma^2 \sim 0.06$) for the system we are studying. For the two-dimensional crystal phase, a semiclassical approximate calculation[3] and a simple Hartree approximation[6] have been reported. For a monolayer of ⁴He on a substrate, a cluster-expansion technique has recently been used by Novaco.[7] A direct comparison with our results is not feasible because of the presence of the substrate potential. It should however be borne in mind that in three dimensions cluster expansions generally give inferior estimates for variational energies[8] as compared with Monte

Carlo calculations. For three-dimensional ⁴He crystals, both approximations are known to be inadequate for quantitative purposes. Since the stable phase is determined on energetic grounds, it is important that energies be calculated accurately in both liquid and crystal phases. As mentioned above, accurate calculations have been reported only for a small low-density region of the liquid phase. Our calculations will not only enable us to determine whether melting or solidification is possible, but will also serve to check the validity of the approximations that have been used.

The model we investigate will be explained in Sec. II. It is a model well tested in three dimensions. Our results will be given in Sec. III, and Sec. IV will be devoted to the discussion and implications to our results.

We remind readers that the proof by Mermin[8] to rule out the existence of two-dimensional crystals at finite temperatures is not applicable when $T = 0$, and thus has nothing to say about our problem. It should also be noted that the absence of crystalline order in two dimensions only occurs when the thermodynamic limit is taken. For two-dimensional systems the limit required in the proof is obtained so slowly that it does not apply to laboratory systems, much less to those modeled in our calculations.

II. MODEL

The Hamiltonian of the system can be written as

$$H = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i \neq j} V(|\vec{r}_i - \vec{r}_j|) , \qquad (2.1)$$

where ∇_i^2 and $\vec{r}_i$ are the two-dimensional Laplacian and the position vector, respectively, and

$$V(r) = 4\epsilon_0\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] , \qquad (2.2)$$

with $\epsilon_0 = 10.22\,^\circ$K and $\sigma = 2.556$ Å.

The trial wave function for the liquid phase is assumed to have the following form

$$\psi_L = \exp\left(-\frac{1}{2}\sum_{i<j} u_{ij}\right), \qquad (2.3)$$

with $u_{ij} = u(r_{ij}) = (b/r_{ij})^5$, b being the variational parameter.

For the crystal phase, a standard localization factor is used so that the wave function takes the form

$$\psi_X = \exp\left(-\frac{1}{2}\sum_{i<j} u_{ij}\right)\prod_{i=1}^{N} h_i$$

$$= \exp\left(-\frac{1}{2}\sum_{i<j} u_{ij}\right)\prod_{i=1}^{N} \exp\left(-\frac{A}{2}(\vec{r}_i - \vec{R}_i)^2\right), \qquad (2.4)$$

where $\{\vec{R}_i\}$ is the set of points in the appropriate triangular lattice. In the crystal phase, both A and b are variational parameters.

The variational wave functions assumed here are of the form used very successfully in the three-dimensional ^{4}He calculations.[9] The Monte Carlo method with periodic boundary conditions are used; systems with 36 and 100 particles are treated. Where some number dependence for the result is suspected, results obtained for the larger system are always presented. In a typical sum where 5×10^5 configurations are involved, the energy is statistically accurate to within 3%.

III. RESULTS

For a given density, one varies the parameters to obtain the lowest energy. Fortunately, one does not have to repeat the Monte Carlo calculations for all densities. Instead, a scaling technique[9] is available to relate the energy at one set of parameters to that at another set. Let $s = (\rho'/\rho)^{1/2}$, $b' = b/s$, and $A' = As^2$. Then

$$\frac{E(\rho', b')}{N} = 2\epsilon_0\left[s^{12}\left\langle\left(\frac{\sigma}{r}\right)^{12}\right\rangle - s^6\left\langle\left(\frac{\sigma}{r}\right)^6\right\rangle\right] + \frac{25\hbar^2 b^5 s^2}{8m}\left\langle\frac{1}{r^7}\right\rangle \qquad (3.1)$$

for the liquid phase, and

$$\frac{E(\rho', b', A')}{N} = 2\epsilon_0\left[s^{12}\left\langle\left(\frac{\sigma}{r}\right)^{12}\right\rangle - s^6\left\langle\left(\frac{\sigma}{r}\right)^6\right\rangle\right]$$

$$+ \frac{25\hbar^2 b^5 s^2}{8m}\left\langle\frac{1}{r^7}\right\rangle + \frac{\hbar^2 s^2 A}{m} \qquad (3.2)$$

for the crystal phase. In terms of the radial distribution function $g(r)$ computed with b, A at density ρ,

$$\left\langle\frac{1}{r^n}\right\rangle = \rho \int g(r)\frac{1}{r^n}d^2r. \qquad (3.3)$$

Since the range of densities of interest is very large, the energy estimates using Eqs. (3.1)–(3.3) may have different variances for different values of s. It is clear that to study possible melting of a two-dimensional crystal, one would like to carry out the variational calculations near the melting density. Since we have no *a priori* knowledge of this density, we pick a reference point in the low-density $(\rho\sigma^2 = 0.234)$ liquid phase. Calculations at this density provide a check against other published work and when carried out over a sufficiently wide range of variational parameters can be used to obtain reasonably accurate values of the energy in the crystallization region. A reference density $(\rho\sigma^2 = 0.8)$ in the crystal regime is chosen and used in the same way. In the present calculations, b is varied between 0.9 and 1.8, and A between 2.0 and 18. After we found the rough shape of energy-vs-density curves in this way we further refined the estimate by carrying out additional variational calculations near the melting density. We find the ranges of parameters for the optimal energy in the density range $0.2 \leq \rho\sigma^2 \leq 0.8$ are $1.15 < b < 1.25$ and $3.0 < A < 12.0$.

Curves of the variational energy vs density for both phases are shown in Fig. 1. Also shown in
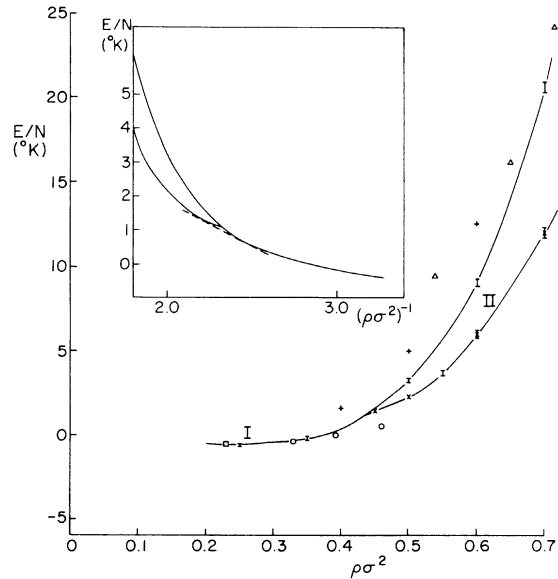

FIG. 1. Energy vs density. I, variational energy for the liquid phase; II, the variational energy for the crystal phase. Also in the figure, open circles, BBGKY results; +, semiclassical calculations; △, the Hartree-approximation results. The insert shows the usual Maxwell double-tangent construction, which establishes the existence of the solid phase.

Fig. 1 are illustrative results of (i) the BBGKY equation with the superposition approximation in the liquid phase,[4] (ii) semiclassical estimates in the crystal phase,[3] and (iii) the Hartree approximation[6] in the liquid phase. The results of previous calculations in the low-density region ($\rho\sigma^2 < 0.33$) are not shown here; they agree with our results to within $0.07\,°K$. Tables I and II give the averages of r^{-6}, r^{-7}, r^{-12} which may be used with the scaling equations (3.1) and (3.2) to calculate the energy at various densities.

Several points of interest can be made from Fig. 1:

(i) The lowest-energy state is in the liquid phase.

(ii) The double-tangent construction shown in the insert of Fig. 1 shows that crystallization takes place at higher densities.

(iii) $\rho\sigma^2 = 0.46$ melting; $\rho\sigma^2 = 0.4$ at solidification.

(iv) As speculated in the introduction, several approximate calculations in the high-density range are not accurate enough to determine the crystallization and melting densities.

(v) In the three-dimensional system, exact variational calculations exist to support the Hartree approximation at very high densities and it was therefore believed that the Hartree approximation would apply in the two-dimensional system[6] near $\rho\sigma^2 = 0.75$, which is the experimentally observed ^{4}He monolayer completion density. However, as shown in the figure, between the melting density ($\rho\sigma^2 = 0.46$) and $\rho\sigma^2 = 0.75$, the Hartree approximation gives poor results. This indicates that though the particles are well localized, the correlations are still strongly dominated by the repulsive potential as manifested by significant lowering of the energy by the Jastrow factor.

Radial distribution functions $g(r)$ at two densities in the liquid phase are shown in Fig. 2; the lower density is near that of the energy minimum, the higher density near the solidification density.

TABLE I. Average values of $\langle\sigma^6/r^6\rangle$, $\langle\sigma^7/r^7\rangle$, and $\langle\sigma^{12}/r^{12}\rangle$ at $\rho\sigma^2 = 0.4$ in the liquid phase.

$\rho\sigma^2$	b	$\langle\sigma^6/r^6\rangle$	$\langle\sigma^7/r^7\rangle$	$\langle\sigma^{12}/r^{12}\rangle$
0.4	1.10	0.427	0.369	0.306
	1.12	0.410	0.350	0.274
	1.14	0.392	0.331	0.236
	1.16	0.376	0.312	0.208
	1.18	0.360	0.296	0.183
	1.20	0.349	0.284	0.165
	1.22	0.336	0.270	0.147
	1.24	0.323	0.256	0.130
	1.26	0.312	0.245	0.118
	1.28	0.301	0.233	0.104
	1.30	0.295	0.227	0.097
	1.32	0.286	0.218	0.088

TABLE II. Average values of $\langle\sigma^6/r^6\rangle$, $\langle\sigma^7/r^7\rangle$, and $\langle\sigma^{12}/r^{12}\rangle$ at $\rho\sigma^2 = 0.45$ in the solid phase.

$\rho\sigma^2$	b	A	$\langle\sigma^6/r^6\rangle$	$\langle\sigma^7/r^7\rangle$	$\langle\sigma^{12}/r^{12}\rangle$
0.45	1.0667	2.0	0.467	0.404	0.338
		3.0	0.420	0.353	0.258
		4.0	0.393	0.324	0.212
		5.0	0.368	0.298	0.179
		6.0	0.347	0.276	0.153
	1.1	2.0	0.442	0.376	0.286
		3.0	0.391	0.321	0.204
		4.0	0.372	0.300	0.173
		5.0	0.360	0.288	0.162
		6.0	0.333	0.261	0.126
		8.0	0.312	0.238	0.103
		10.0	0.292	0.218	0.079
	1.1741	2.0	0.390	0.318	0.185
		3.0	0.364	0.290	0.150
		4.0	0.340	0.266	0.125
		5.0	0.324	0.250	0.108
		6.0	0.313	0.239	0.097

Note that the positions of the first peak of $g(r)$ for the two densities differ by approximately 0.2σ. By contrast, the corresponding difference[10] for three-dimensional ^{4}He at two equivalent densities ($\rho\sigma = 0.328$ at the energy minimum and $\rho\sigma^2 = 0.373$ at solidification) is at most 0.02σ. The larger difference in the peaks of $g(r)$ for the two-dimensional system is undoubtedly due to the larger difference in the two densities. Thus given that the range of liquid densities in two dimensions is larger than that in three, the former is a very useful system to test the validity of theories on strongly interacting Bose liquids.
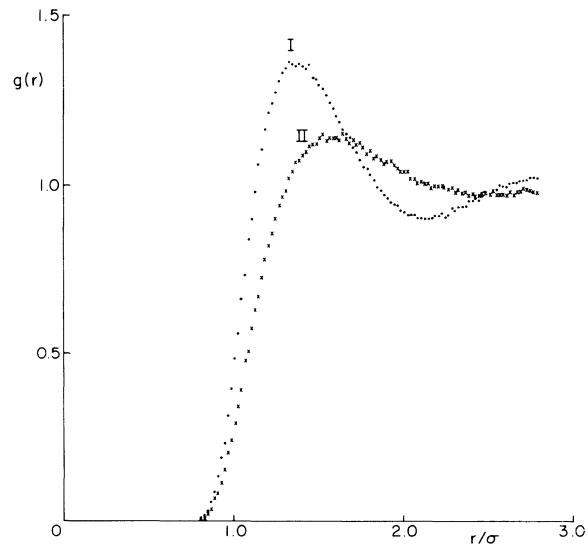

FIG. 2. $g(r)$ for $\rho\sigma^2 = 0.4$, I; and for $\rho\sigma^2 = 0.234$, II.

In the liquid phase, one can easily verify that Reatto's proof[11] of Bose condensation for the class of wave functions given by Eq. (2.3) is still valid in two dimensions. Indeed, we find the condensate fraction at $\rho\sigma^2 = 0.234$ is 0.38, and 0.12 at the solidification density ($\rho\sigma^2 = 0.40$). These condensate fractions are much larger than those found in three dimensions. The differences are sufficiently large (about a factor of 3) that we feel there is a problem here to be investigated.

IV. DISCUSSION

From the set of variational calculations we have presented, we are able to show that the lowest-energy state of the two-dimensional Bose system is a liquid phase, and that it crystallizes only at higher density—as in three dimensions. However, important quantitative differences exist, and we suggest that the present two-dimensional system can be used to test theories on strongly interacting liquids because it covers a much larger range of densities. This fact is already reflected in a demonstration that the inadequacies of certain approximate integral equations used to treat such a system become evident when they are checked for the whole range of liquid densities.

Recent experiments[12] on monolayers of ^{4}He adsorbed on Grafoil showed that melting of a two-dimensional solid occurs at $\rho\sigma^2 = 0.53$. It is very interesting to observe that the melting density of our crystal ($\rho\sigma^2 = 0.46$) at $T = 0$ is close to the observed value. Since the model we used has been

well tested in the three-dimensional Bose system, it is unlikely that the close agreement is purely fortuitous. It is of course true that in the experiment on Grafoil it is not known whether a crystal or disordered solid forms. The experiments were of course carried out at a finite temperature—we do not think that this will have a significant effect on the crystallization density. Our model contains no substrate and this may influence the results. The presence of the substrate potential is believed to be responsible for the observation of a registered phase at a density $\rho\sigma^2 = 0.42$. It also causes the experimentally observed phase diagram to be different from the one reported here. However the experiments by Elgin and Goodstein[11] suggest that only in the low-density region are the properties of the monolayer strongly influenced by the substrate potential. In the high-density region they report that the solid phase and the transitions "seem little affected by the substrate potential once the semiempirical model has been used to remove the effects of substrate inhomogeneity and of second-layer formation." Thus in the high-density region, our modeling of a two-dimensional film without introducing the underlying substrate is likely to be sound. However, we recognize the possibility that the experimental melting density may be somewhat affected by substrate. It is therefore important to carry out similar calculations with a model substrate. Nevertheless the agreement with the measured melting density gives some support to the conjecture that a crystal state is formed in the experiment.

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