A SOLUTION OF THE PERCUS-YEVICK
EQUATION IN TWO DIMENSIONS*

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*Research supported in part by the U.S. Atomic Energy Commission under Contract No. AT(11-1)3498.

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I. INTRODUCTION

At the moment, perturbation theories¹ appear to be the most successful theories for understanding the thermodynamic properties of dense fluids and liquids. Thus far, however, they have not been used for two-dimensional calculations as no readily available reference system exists in two dimensions. Alternately, integral equations may be used to calculate thermodynamic properties and correlation functions; and, of these, the Percus-Yevick (PY) equation has proved to be one of the best. In the remainder of this paper we outline our procedure for solving the PY equation, and check the accuracy of the results.

II. NUMERICAL PROCEDURE

If the PY approximation,

$$c(r) = g(r)[1 - \exp(\beta u(r))], \quad (1)$$

is combined with the Ornstein-Zernike definition of the direct correlation function $c(r)$,

$$G(r) \equiv g(r) - 1 = c(r) + \rho \int c(r') G(|r-r'|) dr', \quad (2)$$

where $\beta = 1/RT$, ρ is the number density and $u(r)$ the intermolecular potential, then one obtains an integral equation for the radial distribution function, $g(r)$. These equations are usually solved either by taking the Fourier Transform of Eq. (2) or by solving the equation in bipolar coordinates. Neither of these methods can be used in two-dimensions so we switched to polar coordinates and evaluated the

integral in Eq. (2) using ten point Gaussian quadrature. Hence, the grid spacings for the angular and radial integrals, necessarily, were multiples of ten. The effect of varying the grid spacing on the accuracy of the calculations is summarized in Table I. In the course of the calculation, it is necessary to interpolate the correlation functions so as to obtain $G(|r-r'|)$. This was done using Stirling's formula with 5th differences. However, instead of $G(r)$, we interpolated the much smoother function

$$h(r) = g(r) \exp[\beta u(r)]. \quad (3)$$

The integral equation was iterated until

$$\epsilon \equiv \left| h(r)_{\text{in}} - h(r)_{\text{out}} \right| \leq 10^{-3}. \quad (4)$$

III. RESULTS

We have checked our numerical technique by comparing our results with Fehder's molecular dynamics calculations. The results are tabulated in Table II. It can be seen that the virial pressures are bad while the internal energy is within 5% of the molecular dynamics results. This is typical of the PY equation and is approximately the same accuracy as exhibited by the PY equation in three dimensions. Thus, as in three dimensions, the PY equation yields correlation functions of sufficient accuracy to obtain good internal energies but not accurate enough to compute the extremely error sensitive virial pressure. We feel that the program is accurate enough to yield much useful information on the theory of surfaces. Several theories of monolayer absorption require a knowledge of the two dimensional radial distribution function.

The two dimensional PY radial distribution functions can be used to test these theories. Work along this line is now in progress.

ACKNOWLEDGMENT

We wish to thank the computer centers at the University of Kansas and the University of Rochester for computer time and R. J. Bearman and Jacob Bigeleisen for their suggestions and encouragement.

TABLE I

The Accuracy of the Program as a Function of Grid Spacing

$\rho^* = 0.6064$

$T^* = 1.645$

	Number of Grid Points				
R	30	30	40	30	40
R'	30	30	40	30	40
θ	20	30	20	40	30
P^*	1.460	1.430	1.454	1.435	1.424
E^*	-.896	-.895	-.897	-.895	-.896
Total core	180K	205K	230K	250K	326K

The machine results are: $\delta P/\rho = 2.286$, $E_1 = -.872$.

TABLE II

Comparison of Percus-Yevick and Molecular Dynamics Data[†]

<u>T[*]</u>	<u>ρ^*</u>	<u>BP/ρ</u>		<u>Energy</u>	
		<u>M.D.</u>	<u>this work</u>	<u>M.D.</u>	<u>this work</u>
1.339	0.4328	1.38	1.09	-0.814	-0.851
1.645	0.6064	2.28	1.44	-0.872	-0.895
1.015	0.5824	1.56	0.89	-1.538	-1.626

[†] The radial integrations were performed with 30 points and the angular integration with 40.