

## AN APPROACH TO TWO-DIMENSIONAL FLUIDS BASED ON THE PERTURBATIONAL METHOD\*

BY W. RUDZIŃSKI AND S. SOKOŁOWSKI

Institute of Chemistry, Maria Curie-Skłodowska University, Lublin\*\*

(Received March 25, 1977)

The perturbational treatment, developed by Weeks, Chandler and Andersen for ordinary bulk phases, is modified here to describe monolayer mobile adsorption.

### 1. Introduction

The theoretical description of two-dimensional fluids arises now great interest in many investigators. This is because of its relation to the large class of interfacial phenomena, which are now extensively investigated for their practical importance. The most popular treatment of interfacial phenomena lies on a mental division of the whole bulk system into three subsystems: two neighbouring bulk phases, and a two-dimensional phase between them. Even with this simplification the problem remains complicated.

It appears, suprisingly, that the two-dimensional counterparts of many theories developed for bulk phases involve a greater degree of complexity than their versions for ordinary bulk phases.

Thus, although Devonshire's adaptation of the LJD cell theory to the two-dimensional case [1] has appeared as long ago as in 1937, no further progress can be noted up to the sixties. The only interesting results was the two-dimensional analogue of the van der Waals model [2].

The first theory advanced was the adaptation of the significant structure theory to two-dimensional case [3, 4]. Actually, there is no analytical solution for Percus-Yevick or Hypernetted Chain equations, but, meanwhile, greatly advanced solutions have been obtained for two-dimensional system of hard discs. Thus Ree and Hoover [5] have obtained a simple, compact equation of state for hard discs, using Pade's approximation. Next, Helfand, Frisch and Lebowitz [6] have constructed a two-dimensional counterpart of the scaled particle theory.

---

\* Dedicated to Professor Kazimierz Gumiński on the occasion of his 70-th birthday.

\*\* Address: Zakład Chemii Teoretycznej, Instytut Chemii, Uniwersytet im. Marii Curie-Skłodowskiej, Nowotki 12, 20-031 Lublin, Poland.

Taking the results of Ree and Hoover, Bergman [7] has proposed a new theory, which also takes attractive interactions in the system into account. Some further progress is due to the work by Ross and Morrison [8], who accounted for the attractive interactions more exactly, but made an error in treating repulsive interactions.

A first Monte Carlo calculations for such systems has been reported by Rosenbluth and Rosenbluth [9], but soon extensive investigations of this kind have been performed by Fehder [10], Tsien and Valleau [11], and Tøxvaerd [12].

Most recent results along these lines have been obtained by Rudziński and Sokołowski [13]. They have discovered the two-dimensional counterpart of the Unit Compressibility Law [14], and on this basis they have performed summation of the virial expansion for the two-dimensional compressibility factor. However, it is known that the unit compressibility law holds satisfactorily only up to the region of liquid densities. So, it is not surprising that the recent theory of Rudziński and Sokołowski shows considerable deviations from experiment (computer simulations) in the region of high densities.

Looking for some other theoretical possibilities, the authors have decided to apply a typical perturbational procedure to the two-dimensional case. In this paper we are going to present our preliminary results obtained by this method.

## 2. Theory

### 2.1. General considerations

One difficulty in applying the perturbational method here is the lack of an analytical solution in the Percus-Yevick theory for hard discs in two dimensions. For this reason the adaptation of such a convenient and rigorous theory as that by Verlet and Weis [15], to two-dimensions is not possible.

The typical procedure in perturbational treatment [16, 17] is to consider the intermolecular potential  $u(r)$ , to be a function of a certain parameter  $\lambda$ , i.e.,  $u(r) = u(r; \lambda)$ . Then  $u(r; 1)$  is the intermolecular potential in our real system, whereas  $u(r; 0)$  is the potential in some reference system, whose quantities will be further denoted by the subscript "0". The most convenient separation of  $u(r; \lambda)$  into "reference" and "perturbed" parts is

$$u(r; \lambda) = u_0(r) + u_1(r), \quad u_0(r) = u(r; 0), \quad u_1(r) = u(r; 1). \quad (1)$$

This, however, is only a general method of separation; the details may differ for various potentials. We shall further accept the method of separation introduced by Weeks, Chandler and Andersen, and denoted here shortly as WCA method [17, 18].

Introducing the reduced quantities  $\varepsilon = \sigma = 1$ , we can write the Lennard-Jones potential in the form

$$u_{\text{LJ}}(r) = 4(r^{-12} - r^{-6}). \quad (2)$$

According to WCA we have

$$u_0(r) = \begin{cases} u_{\text{LJ}}(r) + 1 & \text{for } r < r_m = 2^{1/6} \\ 0 & \text{for } r > r_m \end{cases}$$

$$u_1(r) = \begin{cases} -1 & \text{for } r < r_m \\ u_{\text{LJ}}(r) & \text{for } r > r_m \end{cases} \quad (3)$$

The free energy of the system can be obtained in the usual way. Differentiating and integrating the canonical partition function with respect to  $\lambda$ , we find the exact result

$$F_1 - F_0 = \frac{\beta \rho}{2} \int_0^1 d\lambda \int dr u_1(r) g(r; \lambda). \quad (4)$$

Here  $g(r; \lambda)$  is the radial distribution function when the pair potential is  $u(r; \lambda)$ ,  $F$  is the dimensionless free energy, and subscript "1" denotes the quantities for our real system. If attractive forces have little effected structure of the fluid, then  $g(r; \lambda) = g_0(r)$  and the  $\lambda$  integration is trivial. Thus, within the accuracy to a first perturbational term, the free energy of the system is given by

$$F_1 - F_0 = \frac{\beta \rho}{2} \int dr u_1(r) g_0(r). \quad (5)$$

According to WCA we write the equation for the radial distribution function (rdf)  $g_0(r)$  in the following form

$$g_0(r) = \exp[-\beta u_0(r)] y_{\text{hd}}(r/d_{\text{WCA}}; \eta), \quad (6)$$

where  $y_{\text{hd}}$  is the rdf for a hard disk system, extrapolated smoothly for  $r < d_{\text{WCA}}$ ,  $\eta$  is the packing fraction  $\eta = d_{\text{WCA}}^2 \pi \rho / 4$ , and  $d_{\text{WCA}}$  is the hard-disk diameter, which according to WCA is to be calculated from the condition

$$\int_0^\infty \{\exp[-\beta u_0(r)] - \exp[-\beta u_{\text{hd}}(r)]\} y_{\text{hd}}(r/d; \eta) dr = 0. \quad (7)$$

In the above,  $u_{\text{hd}}$  is the hard-disk potential. The last equation can be reduced by introducing functions [15]

$$(r/d) y_{\text{hd}} = \partial \psi / \partial r, \quad \psi = \sigma_0(r/d - 1) + (1/2!) \sigma_1(r/d - 1)^2 + \dots \quad (8)$$

into the following approximate relation

$$d_{\text{WCA}} = d_{\text{BH}} \left( 1 + \frac{\sigma_1 \delta}{2\sigma_0} \right), \quad (9)$$

where, according to Barker-Henderson [19]

$$d_{\text{BH}} = \int_0^\infty \{1 - \exp[-\beta u_0(r)]\} dr \quad (10)$$

and

$$\delta = \int_0^\infty (r/d_{\text{BH}} - 1)^2 \frac{\partial}{\partial r} \{\exp[-\beta u_0(r)]\} dr. \quad (11)$$

The parameter  $\sigma_0$  can be obtained from Henderson's equation [22], or, from the scaled particle theory. Further  $\sigma_1$  can be very easily evaluated numerically. Table I brings the values of the parameter  $\sigma_0$  evaluated in various ways. Fig. 1 shows  $d_{WCA}$  as a function

TABLE I

The values of  $\sigma_0$  calculated by using different methods

$\eta$	$\sigma_0^a$	$\sigma_0^b$	$\sigma_0^c$	$\sigma_0^d$
0.36276	2.0362	2.0159	2.014	2.058
0.45345	2.683	2.589	2.556	2.683
0.54414	3.666	3.503	3.598	3.637

<sup>a</sup> From equation of Henderson  $\sigma_0 = (1 - 7\eta/16)(1 - \eta)^{-2}$ ; <sup>b</sup> from scaled particle theory  $\sigma_0 = (1 - \eta/2)(1 - \eta)^{-2}$ ; <sup>c</sup> from Percus-Yevick rdf; <sup>d</sup> from Monte Carlo rdf [20].

of temperature. When  $\eta = 0.34$ ,  $d_{WCA}$  and  $d_{BH}$  are practically equal. (In three-dimensional phases it is for  $\eta_{(3d)} = 0.239$  [21].)

When performing other calculations we accepted, for simplicity  $F_0 = F_{hd}$ ,  $Z_0 = Z_{hd}$ , which, obviously, is true only for rather dense phases: First, because this kind of investiga-

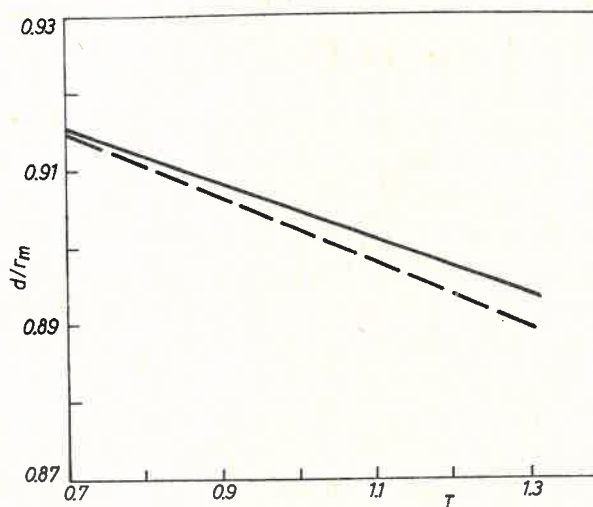


Fig. 1. Temperature dependence of hard disk diameter. Solid line is the WCA criterion, and was calculated for  $\eta = 0.54414$ . The dashed line is the Barker-Henderson criterion

tion was not performed so far; secondly, that we are interest here rather in dense fluids; for moderate densities our recent method based on the unit compressibility law is quite satisfactory.

## 2.2. Hard disk systems

One key characteristic for perturbation treatments is an accurate equation of state for the hard disk reference system. A few years ago Carnahan and Starling have obtained this equation for three-dimensional systems. In a very similar manner Henderson has, recently, obtained its two-dimensional counterpart [22].

$$Z = \frac{1 + \eta^2/8}{(1 - \eta)^2} \quad (12)$$

When expanded into density powers,  $\eta$ , Eq. (12) yields

$$Z = 1 + 2\eta + 3.125\eta^2 + 4.25\eta^3 + 5.375\eta^4 + 6.5\eta^5 + \dots \quad (13)$$

whereas the exact virial expansion has the form [5]

$$Z = 1 + 2\eta + 3.128\eta^2 + 4.2579\eta^3 + 5.3408\eta^4 + 6.3744\eta^5 + \dots \quad (14)$$

Eq. (12) is related to the following equation for the free energy  $F_{\text{hd}}$  in the system of hard discs

$$F_{\text{hd}} = \frac{9\eta/8}{1 - \eta} - \frac{7}{8} \ln(1 - \eta). \quad (15)$$

## 2.3. Perturbational calculations

In order to perform appropriate calculations one has to know the values of the rdf for the hard disk system. As far as we know, there is only one paper giving a few values of it [20]. Therefore we have performed the appropriate calculations in our paper; their results have appeared to be in good accordance with those particular values published

TABLE II  
Radial distribution function for two-dimensional hard-disk system

$r/d$	$\eta$			
	0.37	0.38	0.38	0.40
1.0	2.052	2.1025	2.155	2.209
1.2	1.501	1.523	1.539	1.561
1.4	1.196	1.193	1.191	1.187
1.6	0.942	0.927	0.918	0.904
1.8	0.869	0.859	0.849	0.839
2.0	0.909	0.907	0.905	0.903
2.2	1.026	1.025	1.024	1.022
2.4	1.049	1.056	1.060	1.065
2.6	1.029	1.021	1.019	1.019
2.8	0.991	0.986	0.998	0.972

by Chao Ree and Ree [20]. As to details, we applied Lado's [23] method; our results are given in Table II. Our radial distribution functions have been tabulated up to  $r = 6.0$ . For the values  $\eta \in [0.3, 0.7]$  the corresponding numerical values of virial coefficients in density expansion of rdf were evaluated for every  $r$  with a step 0.025, where the numerical integrations were performed by Simpson's method. The two-dimensional compressibility factor was calculated numerically, according to the following equation

$$Z = Z_{\text{hd}} + \eta \frac{\partial}{\partial \eta} (F_1 - F_{\text{hd}}). \quad (16)$$

The results of our numerical calculations are presented in Table III in comparison with computer simulations. From the above comparison we may conclude that our perturbation theory gives good results at temperatures which are not too low and good results even at

TABLE III  
Comparison of the two-dimensional compressibility factors obtained through computer simulations  $Z_{\text{cs}}$  [10-12], and from Eq. (16)

$T$	$\eta$	$Z_{\text{cs}}$	$Z$ (Eq. (16))
0.655	0.47124	0.585	0.672
0.646	0.51051	0.834	0.869
0.654	0.62832	1.158	1.202
0.95	0.582	$3.05 \pm 0.05$	3.31
0.95	0.423	$2.35 \pm 0.1$	1.98
0.95	0.636	$4.80 \pm 0.07$	5.02
1.436	0.496	2.325	2.21
1.645	0.4762	2.286	2.19
1.441	0.4993	1.591	1.52

the lowest temperatures which are relevant for compressed gases. The discrepancies with computer simulation studies could arise from: neglect of the higher terms in Eq. (5), assumption  $Z_0 = Z_{\text{hd}}$ , errors in the Percus-Yevick estimate of the rdf for the hard disk system.

#### 2.4. Equation of state at low and moderate densities

In our previous paper [13] we have postulated a new physical relationship — two-dimensional unit compressibility law. This relationship was verified by using theoretical two-dimensional virial coefficients for a Lennard-Jones gas. According to this law, in conditions when the two-dimensional compressibility factor is equal to unity, the density of two-dimensional mobile phase is a linear function of temperature

$$\rho = \rho_0(1 - T/T_B). \quad (17)$$

In the above  $T_B$  is two-dimensional Boyle temperature, and is a constant, which can be determined from the second  $B_{(2d)0}$  and third,  $B_{(2d)1}$ , two-dimensional virial coefficients

according to the following relation

$$\rho_0 = \lim_{T \rightarrow T_B} \frac{B_{(2d)0}}{(T/T_B - 1)B_{(2d)1}} \quad (18)$$

This constant for the two-dimensional Lennard-Jones gas is equal to 1.1934. It is interesting to note that it is half of its three-dimensional counterpart, which is equal to 2.397 [14]. Relationship (17) makes possible the summation of the virial expansion for the two-dimensional compressibility factor, since, the existence of relationship (17) allows us to write the following interrelations for the virial coefficients at Boyle temperature

$$B_{(2d)1}(T_B) = B_{(2d)0}^{(1)}(T_d), \quad B_{(2d)2}(T_B) = B_{(2d)1}^{(1)}(T_B) - \frac{1}{2} B_{(2d)0}^{(2)}(T_B) \text{ etc.},$$

$$B_{(2d)n}^{(k)} = \frac{\partial^k}{\partial (T/T_B)^k} (B_{(2d)n}). \quad (19)$$

Assuming that interrelations (19) are valid in some neighbourhood of  $T_B$  we arrive at the following simple equation for the two-dimensional compressibility factor

$$Z = 1 - \pi \rho \int_0^\infty dr r \left\{ \exp \left[ - \frac{u_{LJ}(r)}{T_B(T/T_B - \rho/\rho_0)} \right] - 1 \right\}. \quad (20)$$

TABLE IV

Two-dimensional compressibility factors calculated according to Eq. (20)

$T$	$\rho$	$Z_{cs}$	$Z_A$	$Z$ (Eq. (20))	$Z_{av}$
1.441	0.4993	1.591	1.666	1.203	1.435
1.099	0.4993	1.383	1.378	1.089	1.234
0.880	0.4993	1.079	1.012	1.001	1.006
0.838	0.4993	0.982	0.908	0.966	0.937
1.339	0.4645	1.380	1.480	1.154	1.317
1.145	0.4645	1.261	1.319	1.083	1.201
0.850	0.4645	0.886	0.857	0.931	0.894
0.815	0.4645	0.808	0.769	0.901	0.835
0.95	0.436	0.965 ± 0.023	0.996	0.978	0.987
0.95	0.320	0.880 ± 0.022	0.852	0.913	0.883
0.95	0.245	0.891 ± 0.033	0.830	0.882	0.856
0.7	0.436	0.64 ± 0.005	0.357	0.802	0.579
0.7	0.320	0.566 ± 0.003	0.377	0.750	0.563
0.7	0.245	0.603 ± 0.033	0.465	0.731	0.598
0.7	0.1568	0.729 ± 0.015	0.621	0.770	0.695
0.55	0.320	0.375 ± 0.058	-0.274	0.622	0.174
0.55	0.245	0.349 ± 0.047	-0.019	0.601	0.301
0.55	0.157	0.515 ± 0.037	0.310	0.639	0.474
0.55	0.109	0.615 ± 0.032	0.509	0.695	0.602

$Z_{cs}$  — computer simulations, the data from Refs. [10, 11];  $Z_A$  — results of Andrews [25];  
 $Z_{av} = (Z + Z_A)/2$ .

The last equation is the two-dimensional counterpart of Rudziński's equation for three-dimensional phases [24]. In Table IV the results are shown of our calculations, performed according to Eq. (20), in comparison with those by other authors. It should be noted, that the average value of  $Z$ , obtained from Eq. (20) and equation by Andrews [25] gives excellent agreement with computer simulations.

### 2.5. Adsorption isotherm

Let us assume that the adsorption can be explained as a chemical equilibrium between a three-dimensional Lennard-Jones fluid and a system of particles which vibrate independently of each other, in the direction perpendicular to the surface and where the motion on the surface is given by the equation of state for a two-dimensional Lennard-Jones fluid. Then we have

$$\mu_{(3d)}(\rho_{(3d)}, T) = \mu_{(ad)}(\rho_{(ad)}, T) \cong \mu_{vib}(T) + \mu(\rho, T), \quad (21)$$

where  $\mu$  is the chemical potential as a function of the density and temperature. The subscript ad stands for the subsystem of adsorbed molecules, and 3d for three dimensions. Next, because we can treat the vibrations in the Einstein approximation, they only contribute to the temperature-dependent but density independent term. Making use of the relation  $\partial p / \partial \mu = \rho$ , we obtain the Gibbs adsorption formula

$$\frac{1}{\rho} dp = \left( \frac{\partial \mu}{\partial p_{(3d)}} \right)_T dp_{(3d)}. \quad (22)$$

The last equation can be rearranged as follows

$$d \ln p_{(3d)} = \beta \left( \frac{\partial p}{\partial \rho} \right) \frac{d\rho}{\rho}. \quad (23)$$

This expression must be integrated to obtain the adsorption isotherm. However, a problem arises when we choose lower limits  $p_{3d} = p = 0$  since both integrals become infinite. This problem can be solved by invoking Henry's law behaviour in this limit [26]. Thus,

$$\ln (p_{(3d)}/K_H) = \int_0^{\rho} \left[ \frac{\partial}{\partial \rho} (p\beta) - 1 \right] \frac{d\rho}{\rho} + \ln \rho, \quad (24)$$

where  $K_H$  is Henry's constant [26].

Substituting Eq. (16) into (24) and integrating by parts we have

$$p_{(3d)}/K_H = \mathfrak{S}_{hd}(\eta)\varphi(\eta, T), \quad (25)$$

where

$$\varphi(\eta, T) = \exp \left\{ \frac{\partial}{\partial \eta} [\eta(F_1 - F_{hd})] \right\} \quad (26)$$



and  $\vartheta_{\text{hd}}$  is the adsorption isotherm for the hard-disk system. This isotherm corresponding to scaled particle equation is given by

$$\vartheta_{\text{hd}}(\eta) = \frac{\eta}{1-\eta} \exp \left[ \frac{3\eta - 2\eta^2}{(1-\eta)^2} \right]. \quad (27)$$

The values of  $\vartheta_{\text{hd}}$  are presented in Table V. Fig. 2 presents the adsorption isotherms calculated according to Eq. (25). Inspecting the theoretical isotherms it is evident that the pressure needed to the coverage past  $\eta \cong 0.6$  will be quite large even at low temperatures. Thus we

TABLE V  
The values of  $\vartheta_{\text{hd}}$  calculated according to Eq. (27)

$\eta$	$\vartheta_{\text{hd}}$
0.02	0.0217057
0.04	0.0472964
0.06	0.0776167
0.08	0.1137731
0.10	0.1569942
0.20	0.1569942
0.30	1.8628157
0.40	7.6827533
0.50	54.9811111
0.60	1281.0877
0.70	592283.76

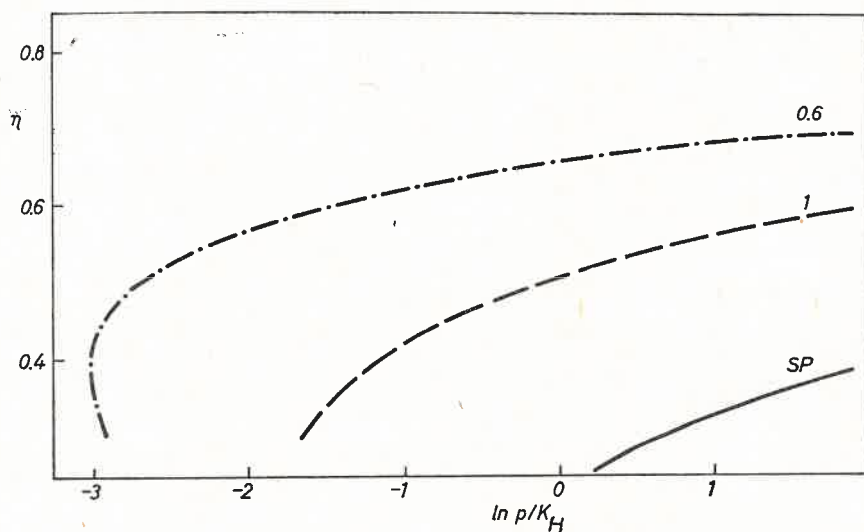


Fig. 2. Adsorption isotherms calculated according to Eq. (25). The long-dashed line was calculated at  $T = 1$ , whereas the dash-dotted line at  $T = 0.6$ . The solid line denotes the  $\vartheta_{\text{hd}}$

can conclude that multilayer formation will occur in preference to further adsorption into monolayer at  $\eta \geq 0.6$ . (It should be stressed that isotherms for other mobile models show analogical behaviour [26].) The critical temperature for the model presented here lies between 0.65 and 0.7. This value is in agreement with previous studies [11, 25].

### 3. Conclusions

We have examined the application of the perturbational method for two-dimensional systems. Even without further improvement the theory gives a better description of the two-dimensional fluids than any existing nonempirical theory. Cell models appear to describe solids rather than fluids. Percus-Yevick or Hypernetted Chain theories of two-dimensional Lennard-Jones fluids are very complicated numerically. Unfortunately, lack of analytical equation for radial distribution function of hard-disk system makes the analytical solution for first-order perturbational term in free energy expansion impossible.

### REFERENCES

- [1] A. D. Devonshire, *Proc. Roy. Soc.* **A163**, 132 (1937).
- [2] T. L. Hill, *Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, Mass. 1960.
- [3] J. J. McAlpin, R. A. Pierotti, *J. Chem. Phys.* **41**, 68 (1964).
- [4] R. A. Pierotti, *Vacuum Microbal. Technol.* **6**, 1 (1969).
- [5] F. H. Ree, H. G. Hoover, *J. Chem. Phys.* **46**, 418 (1967).
- [6] E. Helfand, H. L. Frisch, J. L. Lobewitz, *J. Chem. Phys.* **34**, 1037 (1961).
- [7] E. Bergam, *J. Phys. Chem.* **78**, 405 (1974).
- [8] S. Ross, I. D. Morrison, *Surf. Sci.* **52**, 103 (1975).
- [9] M. N. Rosenbluth, A. W. Rosenbluth, *J. Chem. Phys.* **22**, 881 (1954).
- [10] P. L. Fehder, *J. Chem. Phys.* **50**, 2017 (1969); **52**, 791 (1970).
- [11] F. Tsien, J. P. Valteau, *Mol. Phys.* **27**, 174 (1974).
- [12] S. Toxvaerd, *Mol. Phys.* **29**, 373 (1974).
- [13] W. Rudziński, S. Sokołowski, *Surf. Sci.* **65**, 593 (1977).
- [14] E. M. Holleran, *J. Chem. Phys.* **47**, 5318 (1967); **49**, 39 (1968).
- [15] L. Verlett, J.-J. Weis, *Phys. Rev.* **A5**, 939 (1972).
- [16] G. A. Mansori, F. B. Canfield, *Ind. Eng. Chem.* **62**, 12 (1970).
- [17] J. D. Weeks, D. Chandler, H. C. Andersen, in *Advances in Chemical Physics*, vol. 34, p. 105 ff., Academic Press, New York 1976.
- [18] J. D. Weeks, D. Chandler, H. C. Andersen, *J. Chem. Phys.* **54**, 5237 (1971).
- [19] J. A. Barker, D. Henderson, *J. Chem. Phys.* **50**, 1581 (1969).
- [20] D. G. Chao, F. H. Ree, T. Ree, *J. Chem. Phys.* **50**, 1581 (1969).
- [21] K. E. Gubbins, W. R. Smith, M. K. Tham, E. W. Tjempel, *Mol. Phys.* **22**, 1089 (1971).
- [22] D. Henderson, *Mol. Phys.* **30**, 1581 (1975).
- [23] F. Lado, *J. Chem. Phys.* **49**, 3092 (1969).
- [24] W. Rudziński, *J. Phys.* **A5**, 1642 (1972).
- [25] F. C. Andrews, *J. Chem. Phys.* **64**, 1941 (1976).
- [26] W. A. Steele, *The Interaction of Gases with Solid Surfaces*, Pergamon Press, Oxford 1974.