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ON THE THEORY OF CLASSICAL FLUIDS - III.\*

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SOMMAIRE

On a obtenu des équations intégrales pour les fonctions de corrélation dans les fluides classiques grâce à une méthode due à J.K. Percus. Ces équations sont appliquées à un gaz de molécules à interactions répulsives.

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## I. INTRODUCTION.

In a recent paper<sup>(1)</sup>, Percus has proposed a new derivation of approximate integral equations for the pair distribution of classical fluids. In the present paper, we shall derive and discuss some higher order approximations to the integral equations obtained with Percus' method.

The essential of this method is as follows : we consider the distribution functions in the presence of an external potential  $\psi(r)$ , which will be chosen later on as the potential due to a particle added to the system. The n-particle distribution function in presence of the external potential will then be proportional to the n+1-particle distribution function without the external potential. On the other hand, we choose some arbitrary functional of the distribution functions and of the external potential and we expand it by Taylor's formula around  $\psi = 0$ , the expansion being made as an ascending series in  $\rho(r|\psi) - \rho(r)$ , where  $\rho(r|\psi)$  and  $\rho(r)$  respectively are the one-body distribution functions in the presence and in the absence of the external potential. With this method we can derive integral equations linking the various distribution functions. The accuracy of the approximation depends on the number of terms kept in the Taylor expansion. It is also important for a particular problem to choose in the best possible way the arbitrary functional to be expanded; that is, to choose the functional in such a way that the important effects are taken care of when only the first terms of the Taylor expansion are kept. It remains then to be shown that the contribution of the next terms of the expansion is small. The arbitrariness in the choice of the functional finds its analog in the arbitrariness in the choice of a particular class of diagrams which are summed up in a diagrammatic approach. It seems to us that the advantage of the Percus method is that, once the functional is chosen, the next approximation follows automatically, whereas in a diagrammatic approach there is no absolute criterion for selecting which class of diagrams will come in as a next approximation.

Percus has shown that, with a suitable choice of the functional one may obtain, as a first approximation the so-called Percus-Yevick<sup>(2)</sup> and Hypernetted chain<sup>(3)</sup>

integral equations.

The first aim of this paper is to derive in both cases the integral equations which result when the next term in the Taylor's expansion is taken into account (chapter II). We call them for short PY2 and HCN2 equations.

We then apply these equations to particular models (chapter III) : the hard rod, hard square, hard cube gases, where the cluster integrals involving as much as seven points have been calculated<sup>(4)</sup>. We have calculated the six first virial coefficients for the PY2 equation and the five first virial coefficients in the HCN2 case. This may be compared with the exact result<sup>(4)</sup> and with the same calculation made with the PY and HNC equation without correction<sup>(5)</sup>. Both the PY2 and the HNC2 equations yield exact fourth virial coefficients. This is not so with the uncorrected equations except in the case of the hard rod gas for which the PY equation is exact as shown in Appendix I. When the HNC2 correction is taken into account, the fifth virial coefficient is not much improved. On the other hand, the situation is much more favorable with the PY2 equation : the fifth and sixth virial coefficients remain exact in the hard rod case and take values very near to the exact ones for the hard square and hard cube gases. This is interesting because the hard cube gas simulates fairly well the hard sphere gas, which itself behaves much as a real gas at high temperatures. As it is known<sup>(6)</sup> that, for the hard sphere gas as well as for a real gas at high temperatures, the PY equation is a good first approximation, it is comforting to know that the next term in the Taylor expansion improves the PY result in the hard cube case.

In the low temperature region, no conclusion may be drawn from the present study. But, as it appears that the PY equation deserves a special attention, we have made some calculations for the Argon fluid at low temperatures which complement the few results given in ref.(7). It appears that the internal energies and the pressures yielded by the virial theorem are practically the same as those obtained with the HNC equation, but that the discrepancy between the pressure calculated from the virial theorem and that yielded by the Ornstein-Zernicke relation is much reduced.

## II. DERIVATION OF THE INTEGRAL EQUATIONS.

We shall first recall some definitions and derive some properties of the distribution functions.

The  $n$ -particle distribution function, in the presence of an external potential  $\psi$  is defined in the grand canonical ensemble as :

.../...

$$\rho(1,2 \dots, n | \psi) = \frac{1}{\Xi} \sum_{N \geq n} \frac{z^N}{(N-n)!} \int e^{-\beta U_N} d\vec{r}_{n+1} \dots d\vec{r}_N \quad (1)$$

where  $\Xi$  is the grand partition function :

$$\Xi = \sum_{N \geq 0} \frac{z^N}{N!} \int e^{-\beta U_N} d\vec{r}_1 \dots d\vec{r}_N, \quad (2)$$

$U_N(1,2 \dots N)$  is the N-particle interaction energy, which is the sum of the interparticle potentials  $V(i,j)$  and of the external potential,  $\psi(i)$ .  $z$  is the fugacity.

The various distribution functions  $\rho(1|\psi)$ ,  $\rho(1,2|\psi)$ ,  $\rho(1,2,3|\psi)$  may be obtained by functionally differentiating the grand partition function with respect to the external potential :

$$\frac{\delta \log \Xi}{-\beta \delta \psi(1)} = \rho(1|\psi) \quad (3)$$

$$\frac{\delta^2 \log \Xi}{\beta^2 \delta \psi(1) \delta \psi(2)} = \frac{\delta \rho(1|\psi)}{-\beta \delta \psi(2)} \quad (4)$$

$$= \rho(1,2|\psi) - \rho(1|\psi)\rho(2|\psi) + \rho(1|\psi) \delta(1,2)$$

$$\frac{\delta^3 \log \Xi}{-\beta^3 \delta \psi(1) \delta \psi(2) \delta \psi(3)} = \frac{\delta^2 \rho(1|\psi)}{\beta^2 \delta \psi(2) \delta \psi(3)} \quad (5)$$

$$= \rho(1,2,3|\psi)$$

.../...

$$\begin{aligned}
& - \left\{ (\rho(3|\psi) + \delta(1,3))(\rho(1,2|\psi) - \rho(1|\psi)\rho(2|\psi)) \right. \\
& \quad \left. + \text{same with circ. perm. of } 1,2,3 \right\} \\
& - \rho(1|\psi)\rho(2|\psi)\rho(3|\psi) + \rho(1|\psi)\delta(1,2)\delta(2,3).
\end{aligned}$$

We now define the two and three-body correlation functions,  $S(1,2)$  and  $S(1,2,3)$ , in the absence of the external field : (we shall in the following omit the  $\psi$  when it is put to zero)

$$S(1,2) = \rho(1,2)/(\rho(1)\rho(2)) \quad (6)$$

$$S(1,2,3) = \rho(1,2,3)/(\rho(1)\rho(2)\rho(3)) \quad (7)$$

We also define  $C(1,2)$  the direct correlation function of Ornstein and Zernicke through the relation :

$$-\frac{\beta \delta \psi(2)}{\delta \rho(1)} = \frac{\delta(1,2)}{\rho(1)} - C(1,2) \quad (8)$$

The relation of a functional derivative to its inverse is :

$$\int d\vec{2} \frac{\delta \rho(1)}{\delta \psi(2)} \frac{\delta \psi(2)}{\delta \rho(3)} = \delta(1,3) \quad (9)$$

Using (4) and (8), we obtain an alternative definition of  $C(1,2)$ , the well-known Ornstein-Zernicke relation :

$$S(1,2) = 1 + C(1,2) + \int d\vec{3} C(1,3)\rho(3)(S(3,2) - 1). \quad (10)$$

Now, if we take the external potential as the potential due to a particle added to the system and put it at the point 0, we have :

$$\rho(1|\psi) = \frac{\rho(1,0)}{\rho(0)} \quad (11)$$

$$\rho(1,2|\psi) = \frac{\rho(1,2,0)}{\rho(0)} \quad \text{etc...}$$

Let us now consider a quantity  $f(1,2 \dots n|\psi)$  which is a function of the positions  $1,2 \dots n$  and a functional of  $\psi$ , (and thus of  $\rho(1|\psi)$ ) : as we have said, we shall make the following Taylor's expansion around  $\psi = 0$  :

$$\begin{aligned} f(1,2 \dots n|\psi) &= f(1,2 \dots n) + \\ &+ \int \overrightarrow{dn+1} (\rho(n+1|\psi) - \rho(n)) \left[ \frac{\delta f(1,2 \dots n|\psi)}{\delta \rho(n+1|\psi)} \right]_{\psi=0} + \\ &+ \frac{1}{2!} \int \overrightarrow{dn+1} \overrightarrow{dn+2} (\rho(n+1|\psi) - \rho(n+1)) (\rho(n+2|\psi) - \rho(n+2)) \left[ \frac{\delta^2 f(1,2 \dots n|\psi)}{\delta \rho(n+1|\psi) \delta \rho(n+2|\psi)} \right]_{\psi=0} \end{aligned} \quad (12)$$

We understand immediately how this procedure is used, when we particularize to the two functionals considered by Percus :

a) if we take

$$f(1|\psi) = \rho(1|\psi) e^{\beta\psi}, \quad (13)$$

we have, using (6), (11) and (12) :

.../...

$$\begin{aligned}
\frac{\rho(1,0) e^{\beta V(1,0)}}{\rho(0)} &= \rho(1) + \\
&+ \int a_2^{\vec{}} \rho(2) (s(0,2)-1) (\delta(1,2) + \rho(1) \left[ \frac{\beta \delta \psi(1)}{\delta \rho(2|\psi)} \right]_{\psi=0}) \\
&+ \frac{1}{2} \left[ a_2^{\vec{}} a_3^{\vec{}} \rho(2) \rho(3) (s(0,2)-1) (s(0,3)-1) \times \right. \\
&\quad \left. \times \left[ \delta(1;2) \frac{\beta \delta \psi(1)}{\delta \rho(3|\psi)} + \delta(1,3) \frac{\beta \delta \psi(1)}{\delta \rho(2|\psi)} + \rho(1) \beta^2 \frac{\delta \psi(1)}{\delta \rho(2|\psi)} \frac{\delta \psi(1)}{\delta \rho(3|\psi)} + \right. \right. \\
&\quad \left. \left. + \rho(1) \frac{\beta^2 \delta^2 \psi(1)}{\delta \rho(2|\psi) \delta \rho(3|\psi)} \right]_{\psi=0} \right] \quad (14)
\end{aligned}$$

$$\begin{aligned}
&\times \left[ \delta(1;2) \frac{\beta \delta \psi(1)}{\delta \rho(3|\psi)} + \delta(1,3) \frac{\beta \delta \psi(1)}{\delta \rho(2|\psi)} + \rho(1) \beta^2 \frac{\delta \psi(1)}{\delta \rho(2|\psi)} \frac{\delta \psi(1)}{\delta \rho(3|\psi)} + \right. \\
&\quad \left. + \rho(1) \frac{\beta^2 \delta^2 \psi(1)}{\delta \rho(2|\psi) \delta \rho(3|\psi)} \right]_{\psi=0}
\end{aligned}$$

If we take only the first two terms of the expansion, we find the equation :

$$s(0,1) e^{\beta V(0,1)} = s(0,1) - c(0,1). \quad (15)$$

The use of (15) and (10) to eliminate the direct correlation function  $c(0,1)$  leads to the PY integral equation for the correlation function  $S(0,1)$ .

To calculate the next term in the expansion, so as to obtain the PY2 equation, we must express the second derivative appearing in the square bracket of (14) in terms of the second derivative of  $\rho(1|\psi)$  with respect to  $\psi$ . For this, we use the relation:

$$\frac{\delta^2 \rho(1|\psi)}{\delta \psi(2) \delta \psi(3)} = - \int a_4^{\vec{}} a_5^{\vec{}} a_6^{\vec{}} \frac{\delta^2 \psi(4)}{\delta \rho(5|\psi) \delta \rho(6|\psi)} \times \frac{\delta \rho(1|\psi)}{\delta \psi(4)} \frac{\delta \rho(5|\psi)}{\delta \psi(2)} \frac{\delta \rho(6|\psi)}{\delta \psi(3)} \quad (16)$$

We then need, as may be seen from (5), a relation for the three-body distribution function. This relation is obtained, as was done above for the two-body distribution, by expanding

$$\rho(1,2|\psi) e^{\beta(\psi(1) + \psi(2))}$$

and keeping the first two terms of the expansion :

$$\begin{aligned} \rho(1,2|\psi) e^{\beta(\psi(1) + \psi(2))} &= \rho(1,2) + \\ &+ \int d\vec{3} d\vec{4} \rho(3)(s(0,3) - 1) \left\{ \frac{\delta(\rho(1,2|\psi) e^{\beta(\psi(1) + \psi(2))})}{\delta\psi(4)} \frac{\delta\psi(4)}{\delta\rho(3|\psi)} \right\}_{\psi=0} \end{aligned} \quad (17)$$

Using (5) and (7), we obtain the following linear integral equation for the three body correlation function which is expressed in terms of the two-body functions  $S(1,2)$  and  $C(1,2)$  :

$$\begin{aligned} s(1,2;0) e^{\beta(u(1,0) + u(2,0))} &= s(1,2) + \int d\vec{3} \rho(3) c(0,3)(s(1,2;3) - \\ &- s(1,2)). \end{aligned} \quad (18)$$

The similarity of this equation with the PY equation (15), with (10) taken into account, is striking. The three body correlation function is unfortunately unsymmetrical in view of the special role played by the source particle.

Once we have the three-body correlation function, a straightforward manipulation, using (4), (14) and (16) leads to the equation :

$$s(0,1) e^{\beta v(0,1)} = s(0,1) - c(0,1) + \bar{\Phi}(0,1) \quad (19)$$

where  $\bar{\Phi}(0,1)$  is the correction term calculated as was said above :

.../...

$$\begin{aligned} \bar{\Phi}(0,1) = \frac{1}{2} \int d\vec{2} d\vec{3} \rho(2)\rho(3) c(0,2) c(0,3) s(2,3) & \left\{ \frac{s(2,3;1)}{s(2,3)} (1 - e^{\beta(V(2,1)+V(3,1))}) \right. \\ & \left. - s(1,2)(1 - e^{\beta V(1,2)}) - s(1,3)(1 - e^{\beta V(1,3)}) \right\}. \end{aligned} \quad (20)$$

Using this equation, together with (19), (18) and (10), we may, implicitly, eliminate  $\bar{\Phi}(0,1)$ ,  $s(2,3;1)$  and  $c(0,1)$  and obtain an equation for the two body correlation function which we call the PY2 equation.

Evidently this approximation process can still be carried on further, but things will become quite complicated.

b) Percus has shown that if we take :

$$f(1|\psi) = \log(\rho(1|\psi) e^{\beta\psi}), \quad (21)$$

we obtain as a first approximation the HNC equation. Going to the next order, we find the equation :

$$\log S(0,1) e^{\beta V(0;1)} = S(0,1) - c(0,1) + \bar{\Phi}(0,1), \quad (22)$$

where the correction term is now given by the equation :

$$\begin{aligned} \phi(0,1) = \frac{1}{2} \int d\vec{2} d\vec{3} \rho(2)\rho(3) c(0,2) c(0,3) s(2,3) \times \\ \times \left[ \frac{s(2,3;1)}{s(2,3)} + 1 - \log \frac{s(2,3;1)}{s(2,3)} - S(1,2) + \log S(1,2) - S(1,3) + \log S(1,3) \right] \\ - \frac{1}{2} (S(0,1) - 1 - c(0,1))^2. \end{aligned} \quad (23)$$

The equation for the three-body correlation function is no longer linear but is replaced by an equation of the same type as the HNC equation :

$$\log \frac{S(1,2;0)}{S(1,2)} e^{\beta(v(1,0) + v(2,0))} = \int d\vec{3} \rho(3) c(0,3) \left( \frac{S(1,2;3)}{S(1,2)} - 1 \right). \quad (24)$$

The combination of equations (10), (22), (23) and (24) yields the HNC2 equation for the two body correlation function.

### III. THE VIRIAL EXPANSION AND ITS APPLICATIONS.

We have made series expansion in powers of the density for the PY2 and HNC2 equation. The virial coefficients have been calculated with the help of the compressibility equation :

$$\frac{1}{kT} \frac{\partial p}{\partial \rho} = 1 - \rho \int c(r) d\vec{r} . \quad (25)$$

We have explicitly written down the relevant Ursell diagrams with their weights for the six first virial coefficients in the case of the PY2 equation and the five first virial coefficients in the case of the HNC2 equation. The fourth virial coefficient becomes exact for both equations. As we wish to have some idea of the value of the approximation for the next virial coefficients, we have made a calculation with a specific model. The hard rod, hard square and hard cube gases, for which the cluster integrals we need have been evaluated<sup>(4)</sup> : the virial coefficients which we have calculated are give in table I in the PY2 case, in table II in the HNC2 case. In these tables are also given the corresponding results of the exact calculation<sup>(4)</sup> as well as those yielded by the uncorrected equations<sup>(5)</sup>.

		Hard rod	Hard squares	Hard cubes
4th virial coefficient	exact	1	3.667	11.333
	PY	1	3.778	12.889
	PY2	1	3.667	11.333
5th virial coefficient	exact	1	3.722	3.160
	PY	1	4.236	12.434
	PY2	1	3.639	1.701
6th virial coefficient	exact	1	3.025	-18.879
	PY	1	4.420	9.207
	PY2	1	3.020	-21.203

Table I. Comparison with the exact results of the fourth, fifth and sixth virial coefficients obtained from the PY and PY2 equation for hard rods, squares and cubes.

In Table I, we note the particular situation of the hard rod gas : in that case, the PY equation is exact. This had been conjectured by Hoover and Poirier and is demonstrated in Appendix I. The PY2 equation yields also exact fifth and sixth virial coefficients, and it may be supposed that it is also exact. The improvement due to the use of the PY2 equation is very important both in the two and in the three-dimensional cases. It should be noted that in the calculation of the sixth virial coefficient we have used in the correction term (20) the correlation functions calculated with the lower order PY equation, which is a consistent procedure in this approximation scheme. It turns out that when the functions in front of the square bracket of (20) are replaced by the values calculated from the PY2 equation, the correction is zero in one dimension and amounts in two and three dimension to a **small percentage** of the final result.

		Hard rod	Hard squares	Hard cubes
4th	exact	1	3.667	11.333
virial coefficient	HNC	.9167	2.944	6.630
	HNC2	1	3.667	11.333
5th	exact	1	3.722	3.160
virial coefficient	HNC	.8	1.8041	-6.939
	HNC2	1.0833	4.697	11.706

Table II. Comparison with the exact results of the fourth and fifth virial coefficients obtained from the HNC and HNC2 equation for hard rods, squares and cubes.

The results for the HNC2 equation are given in Table II. We have calculated only the fifth virial coefficient and we may see that the improvement brought about by the correction to the HNC equation is not very important.

#### IV. CONCLUSIONS.

We have shown in this paper that Percus' method can be used to write down explicitly integral equations for the two-body correlation function which generalizes the PY and HNC equation. A first test of the fitness of such equations has been given in the case of the hard cube gas. Further information will be provided in a future paper where the equations given in the present paper will be applied to the case of the lattice gas.

#### Acknowledgments

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APPENDIX I.

The exact correlation function in one dimension is known<sup>(9)</sup> to be :

$$S(x) = \ell \sum_{k=1}^{\infty} \frac{A(x-k)(x-k)^{k-1}}{(\ell-1)^k (k-1)!} \exp\left(-\frac{(x-k)}{\ell-1}\right) \quad (\text{A-1})$$

where  $A(x-k) = 0$  if  $x < 0$

$A(x-k) = 1$  if  $x \geq 0$

and where the length of the hard rod has been taken as length unit.  $\ell$  is the inverse of the density.

We define the following Fourier transform :

$$G(p) = \frac{1}{\ell} \int_{-\infty}^{+\infty} dx \exp(-ipx) (S(x) - 1) \quad (\text{A-2})$$

$$= \frac{\cos p - (\ell-1)p \sin p - 1}{(\ell-1)^2 p^2/2 - (\cos p - (\ell-1)p \sin p - 1)}$$

Using (10) and (A2) we have the Fourier transform  $C(p)$  of the direct correlation function :

$$C(p) = \frac{G(p)}{1 + G(p)} \quad (\text{A-3})$$

$$= \frac{2(\cos p - (\ell-1)p \sin p - 1)}{(\ell-1)^2 p^2}$$

The direct correlation function is given by the Fourier transform of (A-3) :

$$C(x) = - \frac{l}{(l-1)^2} (l-x) \quad \text{if } x < 1$$

(A-4)

$$C(x) = 0 \quad \text{if } x > 1 \quad .$$

The Percus-Yevick equation defined by (10) and (15) is thus satisfied.

APPENDIX II.

We summarize in this Appendix the calculations which have been made using the PY equation in the case of liquid Argon at low temperatures. The technical computation which has been used is the same as in ref.(7). The potential is also the same Lennard Jones potential  $V(r) = 4 \epsilon \left( (\sigma/r)^{12} - (\sigma/r)^6 \right)$ .

The calculation has been made for the following isolated points :

$$T = 84^\circ = 0.70 \epsilon/k, \quad d = 1.4 \text{ gr/cm}^3 = 0.84 \text{ mole}/\sigma^3.$$

$$T = 126^\circ = 1.05 \epsilon/k, \quad d = 1.09 \text{ gr/cm}^3 = 0.66 \text{ mole}/\sigma^3.$$

$$T = 143^\circ = 1.19 \epsilon/k, \quad d = 0.87 \text{ gr/cm}^3 = 0.52 \text{ mole}/\sigma^3.$$

and for two isotherms near the critical point, at

$$T = 153^\circ = 1.28 \epsilon/k \quad \text{and} \quad T = 158^\circ = 1.32 \epsilon/k.$$

The results of these calculations are as follows :

1°) Within the precision of the calculation, the pressures calculated from the virial theorem and the internal energies are the same as those reported in ref.(7). This is even the case when, for the same density and temperature,  $\partial p / \partial \rho$  calculated from the HNC and PY equation differ in sign (this occurs for a part of the 158° isotherm). Thus, we may infer that the critical data determined from the pressures obtained with the virial theorem will be the same as in ref.(7)(see table III).

2°) The values of the compressibility integral differ from the same values calculated with the HNC equation. The discrepancy between the pressures calculated from the virial theorem and from the compressibility formula is substantially reduced. We need only to give one example, as all the results we have got are of the same type : at  $T = 158^\circ$ ,  $d = 0.60 \text{ gr/cm}^3 = 365 \text{ mole}/\sigma^3$ , we get for the compressibility factor  $P / \rho kT$  the value  $z = 0.33$  from the virial theorem (for both equations),  $z = 0.27$  when the Ornstein-Zernicke formula is integrated over the density, in the PY case and  $z = 0.225$

for the same in the HNC case. M. Klein<sup>(8)</sup> has rightly insisted on the fact that there was no compelling reason to prefer the pressures obtained from the virial theorem to those calculated from the compressibility integral, and that the discrepancy between the two was somehow a measure of the inconsistency of the theory. It is from this point of view interesting to compare the critical data obtained using the virial theorem<sup>(7)</sup> (table III, line 2), and those obtained from the compressibility formula : line 3 of table III for the PY case (present study), and line 4 for the HNC case<sup>(8)</sup>.

	$T_c$	$\frac{k T_c}{\epsilon}$	$d_c$ (gr/cm <sup>3</sup> )	$\frac{p_c}{\text{mole}/\sigma^3}$	$\frac{p_c}{p_c k T_c}$	
experiment	151°	1.26	0.536	0.324	0.292	
virial theorem	150°	1.25	0.522	0.315	0.297	
O.Z. {	PY	157°	1.31	0.475	0.29	0.32
	HNC	167°	1.39	0.495	0.30	0.37

Table III. Critical data :

- Line 1 : experiment.
- Line 2 : results obtained when the virial theorem is used (both for the HNC and PY equations).
- Line 3 and 4 : results obtained with the pressure calculated from the Ornstein-Zernicke formula using the PY and HNC equations.

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