

METHOD OF INTEGRAL EQUATIONS IN STATISTICAL THEORY OF LIQUIDS

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Usp. Fiz. Nauk 108, 209—239 (October, 1972)

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1. INTRODUCTION

a) Problem of the theory of the liquid state. The theory of the liquid state of matter is traditionally considered as "insufficiently developed" and "lagging" relative to the theories of gases and solids. With respect to the equilibrium properties of systems, this traditional view should be regarded as obsolete and as not corresponding to the real situation. The theory of classical liquids was intensively developed during the post-war years and made quite noticeable advances during the last few years. If the main task of this statistical theory of matter is taken to be the prediction of the thermodynamic behavior of different systems as functions of the character and details of the intermolecular interaction, then the contemporary accuracy of the solution of this problem for simple liquids is hardly inferior to the accuracy with which we can, for example, calculate theoretically the equation of state of a solid or of a moderately dense gas. Nor are there significant differences, at least when dealing with their equilibrium properties, between the theories of solids, liquids, and gases in the more important physical problem of understanding the molecular mechanism responsible for the observed macroscopic properties of matter.

The main task of calculating the partition function of a system of many bodies is solved in the theory of the liquid state indirectly, by calculating the pair correlation function of the system particles, or the so-called radial distribution function (RDF)  $g(r)$ . The latter is so defined that the expression

$$dw(r) = g(r; T, n) (4\pi r^2 dr/V),$$

where  $V$  is the volume of the entire system, is equal to the probability of observing the centers of two particles spaced  $r$  apart with an uncertainty  $dr$  at a given temperature  $T$  and a particle-number density  $n$  of the system as a whole. The function  $g(r)$  is normalized here so that  $g(r) \rightarrow 1$  as  $r \rightarrow \infty$ . The aforementioned pair correlation function is defined as  $h(r) = g(r) - 1$ , so that

$h(r) \rightarrow 0$  as  $r \rightarrow \infty$ . The function  $g(r)$  or  $h(r)$  describes the internal order in the systems and its dependence on the thermodynamic conditions.

If the function  $g(r; T, n)$  is known, then we can find the thermodynamic functions for monatomic and single-component systems with pair and central interaction between the particles from the well-known exact expressions for the pressure, energy density, and compressibility<sup>[1,2]</sup>:

$$p(T, n) = nkT - (2\pi n^2/3) \int_0^\infty r\Phi'(r) g(r; T, n) r^2 dr, \quad (1)$$

$$\epsilon(T, n) = (3nkT/2) + 2\pi n^2 \int_0^\infty \Phi(r) g(r; T, n) r^2 dr, \quad (2)$$

$$kT (\partial n / \partial p)_T = 1 + 4\pi n \int_0^\infty [g(r; T, n) - 1] r^2 dr, \quad (3)$$

where  $\Phi(r)$  is the molecular potential and  $k$  is Boltzmann's constant. In addition, the Fourier transform of the function  $g(r)$  is directly connected with the angular dependence of the intensity of the coherent scattering of x-rays or slow neutrons by the system<sup>[2,3]</sup>. Thus, for simple liquids, the function  $g(r; T, n)$  describes simultaneously their structure and thermodynamic properties. Therefore the main task of the theory of equilibrium properties of simple liquids is the calculation of the RDF from a specified intermolecular potential  $\Phi(r)$  for all values of  $T$  and  $n$  from the region of existence of the liquid phase. The entire problem can be formulated in exactly the same manner for dense gases.

The radial distribution function is defined formally in the form of a multiple integral of the total Gibbs distribution function of all the system particles in coordinate space<sup>[1,2]</sup>

$$g(|r_1 - r_2|) = (V^2/Q_N) \int_V \dots \int_V \exp[-U_N(r_1, \dots, r_N)/kT] dr_3 \dots dr_N, \quad (4)$$

$$Q_N = \int_V \dots \int_V \exp[-U_N(r_1, \dots, r_N)/kT] dr_1 \dots dr_N, \quad (5)$$

where  $U_N$  is the total interaction energy of the system particles

$$U_N(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{1 \leq i < j \leq N} \Phi(|\mathbf{r}_i - \mathbf{r}_j|). \quad (6)$$

It is assumed in (4) and (5) that ultimately the limit will be taken as  $N \rightarrow \infty$  and  $V \rightarrow \infty$  at  $n = N/V = \text{const}$ . A similar expression for the grand canonical ensemble is given below (see Eq. (13)). The problem of determining the function  $g(\mathbf{r}; T, n)$  reduces therefore to the problem of calculating or asymptotically estimating the integrals (4) and (5) or the sums (13). For gases, this problem is solved by the Mayer group integral method<sup>[4,5]</sup> (page 415 of the Russian translation), which leads to an expansion of the function  $g(\mathbf{r})$  in an infinite series in integer powers of the density  $n$  and accordingly to the so-called virial series for the thermodynamic functions. For realistic potentials  $\Phi(\mathbf{r})$ , only the first few terms of such series are known, and the results are applicable only to low-density gases. The only exception is the model problem of hard spheres, for which the first seven terms of the virial series for the pressure are known<sup>[6]</sup>. For liquids and high-density gases, the integrals of the type (2) and (5) can be directly estimated by the Monte Carlo method (MC) using high-speed computers<sup>[7,8]</sup>. Interesting results were obtained by this method for the model hard-sphere system and for a system of particles interacting via a Lennard-Jones potential.

There is no need for estimating the complicated multiple integrals (4) and (5) in the molecular dynamics method (MD), which also involves the use of high-speed computers. A "mathematical experiment" is performed here on a model system of particles by calculating the trajectories and velocities of all the particles over a long periods of time, followed by the determination of various averaged equilibrium and kinetic characteristics of the system<sup>[7,9-11]</sup>. There are well-known good results for the hard-sphere system and for the system of particles with Lennard-Jones interaction. Both computer methods, the MC method and the MD method, can yield in principle numerical results of very high accuracy, but various errors creep into the actual calculations, due mainly to the practical need for confining oneself to a small number of particles in the principal cell and to the finite duration of the trajectories. Nonetheless, the estimates of the statistical properties of model liquid or dense-gas systems by these methods must be regarded at present as the most accurate. A certain inconvenience in the analysis of the calculation results is that the latter are presented in the form of tables or diagrams, and there are no analytic expressions.

b) The method of integral equations. A special position is occupied by another method of solving the main problem of the theory of liquids, namely the search for approximate integral equations for the RDF  $g(\mathbf{r}; T, n)$  when the potential  $\Phi(\mathbf{r})$  is specified. It is seen from (4)–(9) that if the parameters  $T$  and  $n$  are specified, then the RDF is determined uniquely by the function  $\Phi(\mathbf{r})$ , viz.,  $g(\mathbf{r}) = G\{T, n; \Phi\}$ , so that it is likely that there exists an integral equation in closed form, perhaps a very complicated one, relating these two functions. Searches for such an equation have been going on

since 1935, when Kirkwood and Yvon first proposed a very simplified variant of an integral relation between  $g(\mathbf{r})$  and  $\Phi(\mathbf{r})$ <sup>[12,13]</sup>. By now, several such approximate equations are known, with different degrees of accuracy. The method of integral equations in the theory of liquids is attractive because of two circumstances: the possibility of obtaining analytically representable results concerning the structure and thermodynamic properties of simple liquids, and the possibility of solving the inverse problem, that of reconstructing the form of the intermolecular potential  $\Phi(\mathbf{r})$  if the function  $g(\mathbf{r})$  is known, say, from precision x-ray measurements.

The first serious progress in the method of integral equations was made when Kirkwood<sup>[14]</sup>, Bogolyubov<sup>[1]</sup>, and Born and Green<sup>[15]</sup> proposed two variants of a nonlinear integral equation for the function  $g(\mathbf{r})$  using Kirkwood's well-known superposition approximation

$$F_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g(|\mathbf{r}_1 - \mathbf{r}_2|) g(|\mathbf{r}_1 - \mathbf{r}_3|) g(|\mathbf{r}_3 - \mathbf{r}_2|)$$

to close the infinite chain of integro-differential equations for the reduced distribution functions  $F_s(\mathbf{r}_1, \dots, \mathbf{r}_s)$ ,  $s = 1, 2, \dots$ ,  $F_2(\mathbf{r}_1, \mathbf{r}_2) \equiv g(|\mathbf{r}_1 - \mathbf{r}_2|)$ . In the Bogolyubov form, this equation, henceforth designated BBGKY, is

$$kT \ln g(r) + \Phi(r) + (2\pi n/r) \int_0^\infty [g(\rho) - 1] \left[ \int_{|r-\rho|}^{r+\rho} \mathcal{E}(t) t dt \right] \rho d\rho = 0, \quad (7)$$

where

$$\mathcal{E}(t) = \int_{-\infty}^t \Phi'(x) g(x) dx. \quad (8)$$

An investigation of the solutions of this equation and of their thermodynamic consequences have shown that it is not accurate enough when it comes to numerical estimates of the properties of real simple liquids, but provides a correct qualitative description<sup>[2,16,17]</sup>.

We shall not dwell on other attempts to obtain more accurate equations for the function  $g(\mathbf{r})$ , and proceed directly to the most important results. In 1958, Percus and Yevick, attempting to introduce collective coordinates for the description of the dynamics of a liquid as a many-body system, proposed a new nonlinear integral equation for the RDF<sup>[18]</sup>. Its derivation and justification are based on intuitive physical considerations and inaccurate approximations. If account is taken furthermore of the extreme simplicity of the Percus-Yevick equation (PY), it was surprising that its solution yielded for model liquids data that compared favorably with other known results. In addition, perfectly satisfactory agreement with the experimental data was obtained for real simple liquids such as liquid argon. In a subsequent paper, Percus<sup>[19]</sup> proposed a more serious derivation of this equation, using a procedure in which the functionals were expanded in functional series. It was demonstrated that it is possible to obtain an entire family of approximate linear integral equations for the function  $g(\mathbf{r})$ , of the same type as the initial PY equation, from which the best can be chosen. In particular, it became possible to obtain by this method, besides the PY equation itself, also the Kirkwood-Bogolyubov equation (KB) (7)–(8) and the equation of hyper-netted chains<sup>[20-23]</sup>, which was already known by that time (see below). In addition, it turned out that the method proposed in<sup>[19]</sup> paves the way for the construction of higher

approximations and refinements of the resultant integral equations for the function  $g(r)$ , something missing from the preceding theories.

The purely outward aspect of approximations of the PY type can be explained and illustrated in a very simple manner. We introduce, following the classical paper of Ornstein and Zernike<sup>[24]</sup>, together with the "complete" two-particle correlation function  $h(r) = g(r) - 1$ , also the so-called "direct" correlation function  $C(r)$ , which is connected with  $h(r)$  by the relation

$$C(r) = h(r) - n \int h(|r - \rho|) C(\rho) d\rho. \quad (9)$$

Regardless of the initially proposed meaning of the function  $C(r)$ , we shall treat it as an auxiliary function, for which expression (9) is the definition. Then the required integral equation for  $g(r)$  could be obtained if we were able to find one more connection between the functions  $C(r)$  and  $g(r)$ . All the known lower-order approximations correspond to assumptions that there is a simple connection between the function  $C(r)$  and  $g(r)$ . Thus, the PY equation is obtained under the assumption

$$C(r) \approx g(r) (1 - e^{\Phi(r)/kT}), \quad (10)$$

and the equation of the hyper-netted chains is obtained with the approximation

$$C(r) \approx g(r) - 1 - \ln g(r) - (\Phi(r)/kT). \quad (11)$$

Both approximations satisfy the general requirements with respect to the asymptotic behavior of the functions  $g(r)$  and  $C(r)$  as  $r \rightarrow \infty$ . Substituting expression (10) or (11) in the Ornstein-Zernike (OZ) equation (9), we obtain closed nonlinear integral equations for the function  $g(r)$ , the PY equation, and the equation of the superentwined chains, respectively. The accuracy of the employed approximation can be verified and established only after solving the obtained integral equation. In this approach, there is obviously no regular method for constructing approximations of the type (10) or (11). This arbitrariness is partially eliminated in Percus' method of functional expansions.

An important role was played by the publication of a paper by Stell<sup>[25]</sup>, who has shown that all the approximations of the described type can be obtained by summing an infinite sequence of diagrams describing the complete set of all the interactions in the system in a graphic representation of the Mayer group integral method. Stell assumes that all the closed results that can be obtained in the theory of liquids by complete or partial summation of the Mayer series should be valid for a liquid, from analytic-continuation considerations, regardless of the convergence radius of the initial series. Actually, the equation of the method of hyper-netted chains was indeed obtained first by a diagram method, even prior to the publication of<sup>[25]</sup>, and was named after the type of the summed diagrams. This equation contains also a sum of a larger number of diagrams than the PY equation.

The topological method of partial summation of diagrams and the Percus analytic method of functional expansions turned out to be equivalent. The method of functional expansions has the advantage that it allows one to go to higher approximations for the integral equations of the initial approximation, whereas in the

diagram method there is no reliable method of selecting the higher-approximation diagrams. In addition, direct summation of a sequence of higher-approximation diagrams entails very great difficulties and is rarely realizable. Finally, we note that functional expansions make it possible to obtain exact upper and lower bounds for the thermodynamic quantities by estimating the residual term of the expansion<sup>[26]</sup>.

The method of approximate integral equations for the RDF has recently become very widely used, and has led to significant progress in the theory of equilibrium properties of simple liquids. Many papers have been published and continue to be published on this subject in the foreign literature, especially on the PY equation, its solutions, refinements, and applications. These equations are hardly touched upon in the Soviet physics literature. In the next two chapters of this review we present a critical exposition of the theory and results of the integral-equation method in the theory of simple liquids and dense gases. We shall adhere to the formalism of functional expansions and will not discuss diagram methods. Principal attention will be paid to the most popular and the simplest PY equation.

## 2. THE PERCUS-YEVICK EQUATION

a) **Functional definition of the direct correlation function.** Before we proceed to derive and discuss approximate equations of the PY type, let us consider certain rigorous relations for the correlation functions of a classical system of particles; these relations will be needed later on. We have in mind the connection between the correlation functions and the functional derivatives of the partition function with respect to the external field. For a canonical ensemble of systems, these connections have been known for a long time<sup>[1,27]</sup>. It will be more convenient for us to adhere to the formalism of the grand canonical ensemble, and we shall follow mainly the exposition of<sup>[28]</sup>. Our aim is to obtain a functional determination of the already mentioned direct correlation function  $C(r)$ .

Let  $F_s(\mathbf{r}_1, \dots, \mathbf{r}_s)$ ,  $s = 1, 2, \dots$ , be a set of reduced ("partial") distribution functions in coordinate space for groups of  $s$  particles in a many-particle system occupying a volume  $V$ . We normalize the function  $F_s$  by the condition

$$V^{-s} \int \dots \int F_s(\mathbf{r}_1, \dots, \mathbf{r}_s) d\mathbf{r}_1 \dots d\mathbf{r}_s = 1. \quad (12)$$

If the function  $F_s$  is referred to a grand canonical ensemble, then we get in place of expressions of the type (4)–(5)

$$n^s F_s(\mathbf{r}_1, \dots, \mathbf{r}_s) = \frac{1}{\Xi} \sum_{N=s}^{\infty} [z^N / (N-s)!] \int \dots \int \exp(-U_N/kT) d\mathbf{r}_{s+1} \dots d\mathbf{r}_N, \quad (13)$$

where  $\Xi$  is the grand partition function

$$\Xi = \sum_{N=0}^{\infty} (z^N / N!) \int \dots \int \exp(-U_N/kT) d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (14)$$

where  $n = \bar{N}/V$  is the average particle-number density and  $z$  is the activity connected with the chemical potential  $\mu$  by the relation

$$z = (mkT/2\pi\hbar^2)^{3/2} \exp(\mu/kT).$$

In (12)–(14) it is implied through that the limit as  $V, \bar{N} \rightarrow \infty$  at  $n = \text{const}$  will ultimately be taken. In the absence of external forces, the energy  $U_N(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is defined as in Eq. (6), and owing to the homogeneity and isotropy of the system we have for the lower-order functions  $F_S$  in the thermodynamic limit

$$F_1(\mathbf{r}_1) = 1, \quad F_2(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|) \quad \text{etc.} \quad (15)$$

In the more general case, the system can be situated in a specified external field  $\psi(\mathbf{r})$ . We then have for the energy in place of (6)

$$U_N(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{1 \leq i < j \leq N} \Phi(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{1 \leq i \leq N} \psi(\mathbf{r}_i),$$

and the simple properties (15) are no longer obtained. The functions  $F_S$  now turn out to be functionals of  $\psi(\mathbf{r})$  and have a lower spatial symmetry. To emphasize this circumstance and to be able to distinguish the functions  $F_S$  in an external field from the ‘‘unperturbed’’ functions  $F_S$ , we shall explicitly indicate the functional argument and write  $F_S(\mathbf{r}_1, \dots, \mathbf{r}_S | \psi)$  and  $F_S(\mathbf{r}_1, \dots, \mathbf{r}_S | 0)$  respectively.

The grand partition function  $\Xi$  now also turns out to be a functional of  $\psi(\mathbf{r})$ ,  $\Xi = \Xi\{\psi\}$ . Let the external field undergo a small change by an amount  $\delta\psi(\mathbf{r})$ . Then, as follows from (14), we can find

$$-kT\delta \ln \Xi / \delta\psi(\mathbf{r}_1) = nF_1(\mathbf{r}_1 | \psi).$$

Analogously, by varying this expression once more with respect to the external field  $\psi(\mathbf{r})$  at another point  $\mathbf{r} = \mathbf{r}_2$ , taking into account the explicit expression obtainable from (13) for  $F_1(\mathbf{r}_1 | \psi)$ , we get

$$\begin{aligned} (-kT)^2 \delta^2 \ln \Xi / \delta\psi(\mathbf{r}_1) \delta\psi(\mathbf{r}_2) &= -kT\delta(nF_1(\mathbf{r}_1 | \psi)) / \delta\psi(\mathbf{r}_2) \\ &= nF_1(\mathbf{r}_1 | \psi) \delta(\mathbf{r}_1 - \mathbf{r}_2) + n^2[F_2(\mathbf{r}_1, \mathbf{r}_2 | \psi) - F_1(\mathbf{r}_1 | \psi) F_1(\mathbf{r}_2 | \psi)]. \end{aligned} \quad (16)$$

The right-hand side of this equation contains the complete two-body correlation function in the presence of an external field. In the same manner, by subsequent functional differentiation with respect to the external field, we can express any many-body correlation function in terms of the functional derivatives of  $\ln \Xi$  with respect to  $\psi(\mathbf{r})$  of the appropriate higher order. For ordinary ‘‘unperturbed’’ correlation functions we must assume that the external field is only virtual and put  $\psi(\mathbf{r}) = 0$  after calculating the functional derivatives, for example,

$$-kT\delta \ln \Xi / \delta\psi(\mathbf{r}_1) |_{\psi=0} = nF_1(\mathbf{r}_1 | 0) \quad \text{etc.}$$

If we refer the reduced distribution functions  $F_S$  to the canonical ensemble, then the same results are obtained by functional differentiation of the quantity  $\ln Z_N\{\psi\}$  in place of  $\ln \Xi\{\psi\}$  with respect to the external field, where  $Z_N\{\psi\}$  is the canonical partition function of the system in the external field  $\psi$ . In any ensemble, the generating functional for the correlation functions is the quantity  $-A\{\psi\}/kT$ , where  $A\{\psi\}$  is the free energy (the thermodynamic potential) of the corresponding ensemble in the external field.

Let us explain now how to introduce the functional definition of the ‘‘direct’’ OZ correlation function  $C(\mathbf{r})$ . To this end, we consider the functional identity

$$\int [\delta\psi(\mathbf{r}_1) / \delta(nF_1(\mathbf{r}_3 | \psi))] [\delta(nF_1(\mathbf{r}_3 | \psi)) / \delta\psi(\mathbf{r}_2)] d\mathbf{r}_3 = \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (17)$$

If we substitute here the value of the second integrand factor from (16), we note that the function  $\delta\psi(\mathbf{r}_1) / \delta(nF_1(\mathbf{r}_2 | \psi))$  contains a term that is singular at  $\mathbf{r}_1 = \mathbf{r}_2$ . We separate this term, putting

$$(kT)^{-1} \delta\psi(\mathbf{r}_1) / \delta(nF_1(\mathbf{r}_2 | \psi)) = C(\mathbf{r}_1, \mathbf{r}_2 | \psi) - [\delta(\mathbf{r}_1 - \mathbf{r}_2) / nF_1(\mathbf{r}_2 | \psi)].$$

Taking this into account, Eq. (17) leads to an equation for  $C(\mathbf{r}_1, \mathbf{r}_2 | \psi)$

$$\begin{aligned} n_1(\mathbf{r}_1 | \psi) F_1(\mathbf{r}_2 | \psi) C(\mathbf{r}_1, \mathbf{r}_2 | \psi) &= \\ &= F_2(\mathbf{r}_1, \mathbf{r}_2 | \psi) - F_1(\mathbf{r}_1 | \psi) F_1(\mathbf{r}_2 | \psi) - nF_1(\mathbf{r}_1 | \psi) \\ &\times \int C(\mathbf{r}_1, \mathbf{r}_3 | \psi) [F_2(\mathbf{r}_2, \mathbf{r}_3 | \psi) - F_1(\mathbf{r}_2 | \psi) F_1(\mathbf{r}_3 | \psi)] d\mathbf{r}_3. \end{aligned} \quad (18)$$

Putting now  $\psi = 0$  and denoting  $C(\mathbf{r}_1, \mathbf{r}_2 | 0) = C(|\mathbf{r}_1 - \mathbf{r}_2|)$ , we find, taking the properties (15) into account, that Eq. (18) at  $\psi = 0$  coincides with (9). The function  $C(\mathbf{r}_1, \mathbf{r}_2 | \psi)$  defined by the integral equation (18) can therefore be regarded as a natural generalization of the OZ correlation function  $C(\mathbf{r})$  to include the case when an external field is present.

Thus, we have for the ‘‘direct’’ correlation function  $C(\mathbf{r})$  the functional definition

$$- (kT)^{-1} \delta\psi(\mathbf{r}_1) / \delta(nF_1(\mathbf{r}_2 | \psi)) |_{\psi=0} = n^{-1} \delta(\mathbf{r}_1 - \mathbf{r}_2) - C(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (19)$$

This is analogous to the result (16) in the absence of a field:

$$-kT\delta(nF_1(\mathbf{r}_1 | \psi)) / \delta\psi(\mathbf{r}_2) |_{\psi=0} = n\delta(\mathbf{r}_1 - \mathbf{r}_2) + n^2[g(|\mathbf{r}_1 - \mathbf{r}_2|) - 1].$$

We see therefore that the function  $C(\mathbf{r})$  should more readily be called not the ‘‘direct’’ but the ‘‘inverse’’ correlation function.

b) **The Percus approximation.** We consider an arbitrary function of two variables  $f(u, v)$  with sufficiently simple properties in the vicinity of the point  $(u = 1, v = 0)$ , and construct with its aid the functional

$$\Pi\{\psi(\mathbf{r})\} = f(F_1(\mathbf{r} | \psi), \psi(\mathbf{r})). \quad (20)$$

At  $\psi = 0$  we have  $F_1(\mathbf{r} | 0) = 1$  and  $\Pi\{0\} = f(1, 0)$ . If we assume the external field to be weak, we can expand the functional  $\Pi\{\psi\}$  into a functional Taylor series in powers of the deviation of the single-particle distribution function from the homogeneous distribution:

$$\begin{aligned} \Pi\{\psi\} &= \Pi\{0\} + \int [\delta\Pi\{\psi(\mathbf{r}')\} / \delta F_1(\mathbf{r}' | \psi)]_{\psi=0} [F_1(\mathbf{r}' | \psi) - 1] d\mathbf{r}' \\ &+ (1/2) \iint [\delta^2\Pi\{\psi\} / \delta F_1(\mathbf{r}' | \psi) \delta F_1(\mathbf{r}'' | \psi)]_{\psi=0} \\ &\times [F_1(\mathbf{r}' | \psi) - 1] [F_1(\mathbf{r}'' | \psi) - 1] d\mathbf{r}' d\mathbf{r}'' \quad (21) \end{aligned}$$

If the convergence of this series is good, which for a specified  $\psi$  depends on the choice of the function  $f(u, v)$  in (20), then we can confine ourselves approximately to a small number of the terms in the series and obtain by the same token for the functional  $\Pi\{\psi(\mathbf{r})\}$  an approximate representation which is linear, quadratic, etc. in powers of the deviation of  $F_1(\mathbf{r} | \psi)$  from unity.

We confine ourselves for the time being to the linear approximation in the series (21). From (20) we have

$$\begin{aligned} \delta\Pi\{\psi(\mathbf{r}')\} / \delta F_1(\mathbf{r}' | \psi) |_{\psi=0} &= \delta f(F_1(\mathbf{r}' | \psi), \psi(\mathbf{r}')) / \delta F_1(\mathbf{r}' | \psi) |_{\psi=0} \\ &= \partial f / \partial u |_{u=1, v=0} \delta(\mathbf{r} - \mathbf{r}') + \partial f / \partial v |_{u=1, v=0} \delta\psi(\mathbf{r}) / \delta F_1(\mathbf{r}' | \psi) |_{\psi=0}. \end{aligned}$$

Using (19), we get

$$\begin{aligned} \delta\Pi\{\psi(\mathbf{r}')\} / \delta F_1(\mathbf{r}' | \psi) |_{\psi=0} &= \\ &= (\partial f / \partial u - kT \partial f / \partial v) |_{u=1, v=0} \delta(\mathbf{r} - \mathbf{r}') + nkT \partial f / \partial v |_{u=1, v=0} C(|\mathbf{r} - \mathbf{r}'|), \end{aligned}$$

where  $C(\mathbf{r})$  is the ‘‘direct’’ correlation function, and substitution in (21) leads to a linear approximation in

the form

$$f(F_1(\mathbf{r}|\psi), \psi(\mathbf{r})) = f(1, 0) + \left. \frac{\partial f}{\partial u} - kT \frac{\partial f}{\partial v} \right|_{u=1, v=0} [F_1(\mathbf{r}|\psi) - 1] + kT \left. \frac{\partial f}{\partial v} \right|_{u=1, v=0} \int C(|\mathbf{r} - \mathbf{r}'|) [F_1(\mathbf{r}'|\psi) - 1] d\mathbf{r}'. \quad (22)$$

We shall call such an approximation the Percus approximation.

The main idea of the PY method is that the external field  $\psi(\mathbf{r})$  in (22) is chosen to be the molecular field  $\Phi(|\mathbf{r} - \mathbf{r}_0|)$  of the "extra" particle, which is of the same type as the remaining particles of the system and is located at the point  $\mathbf{r}_0$ .<sup>1)</sup> For a canonical ensemble this means a transition from a system of  $N$  particles at the points  $\mathbf{r}_1, \dots, \mathbf{r}_N$  at  $\psi = 0$  to a system of  $N + 1$  particles at point  $\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N$  at  $\psi(\mathbf{r}) = \Phi(|\mathbf{r} - \mathbf{r}_0|)$ , and analogously for each term of the grand canonical ensemble. Then

$$U_N(\mathbf{r}_1, \dots, \mathbf{r}_N | \Phi) = U_{N+1}(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N),$$

and consequently

$$F_s(\mathbf{r}_1, \dots, \mathbf{r}_s | \Phi) = F_{s+1}(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_s)$$

for all  $s = 1, 2, \dots$ . At  $s = 1$  we obtain  $F_1(\mathbf{r}|\Phi) = g(|\mathbf{r} - \mathbf{r}_0|)$ , and substitution in (22) yields

$$f(g(|\mathbf{r} - \mathbf{r}_0|), \Phi(|\mathbf{r} - \mathbf{r}_0|)) = f(1, 0) + \left. \frac{\partial f}{\partial u} - kT \frac{\partial f}{\partial v} \right|_{u=1, v=0} [g(|\mathbf{r} - \mathbf{r}_0|) - 1] + kT \left. \frac{\partial f}{\partial v} \right|_{u=1, v=0} \int C(|\mathbf{r} - \mathbf{r}'|) [g(|\mathbf{r}' - \mathbf{r}_0|) - 1] d\mathbf{r}'. \quad (23)$$

It is assumed here implicitly that the perturbation due to the introduction of the "extra" particle into the system can be regarded as small for correlation functions of all ranks. Comparing (23) with (9) we obtain an estimate for the "direct" correlation function in the Percus approximation

$$kT \left. \frac{\partial f}{\partial v} \right|_{u=1, v=0} C(\mathbf{r}) = \left. \frac{\partial f}{\partial u} \right|_{u=1, v=0} [g(\mathbf{r}) - 1] - f(g(\mathbf{r}), \Phi(\mathbf{r})) + f(1, 0), \quad (24)$$

where we have put  $\mathbf{r}_0 = 0$ . Actually, we obtain here an entire class of approximate estimates that depend on the choice of the functions  $f(u, v)$ . Subsequent substitution of  $C(\mathbf{r})$  from (24) into the exact equation (9) leads to a class of approximate closed nonlinear integral equations for RDF  $g(\mathbf{r})$ , namely equations of the PY type.

The approximation (24) ensures, for any choice of the function  $f(u, v)$ , the correct asymptotic behavior of the function  $C(\mathbf{r})$  as  $r \rightarrow \infty$ . In this case we have  $\Phi(\mathbf{r}) \rightarrow 0$  and  $g(\mathbf{r}) \rightarrow 1$ , and independently of the manner in which the limit  $g(\mathbf{r}) \rightarrow 1$  is taken and the function  $f(u, v)$  is chosen, we obtain from (24)

$$C(\mathbf{r}) \approx -\Phi(\mathbf{r})/kT \quad (r \rightarrow \infty), \quad (25)$$

which is the exact result<sup>[30]</sup>.

The choice of the functions  $f(u, v)$  in (24) can be limited by requiring a good description of the properties of not too dense a gas. It is known that the first term of the exact expansions of the functions  $g(\mathbf{r})$  and  $C(\mathbf{r})$  in powers of the density are<sup>[1,2,4]</sup>

$$g(\mathbf{r}) = e^{-\Phi(\mathbf{r})/kT} [1 + n \int \chi(\mathbf{r} - \mathbf{r}') \chi(\mathbf{r}') d\mathbf{r}' + \dots], \quad (26)$$

$$C(\mathbf{r}) = \chi(\mathbf{r}) [1 + n \int \chi(\mathbf{r} - \mathbf{r}') \chi(\mathbf{r}') d\mathbf{r}' + \dots], \quad (27)$$

<sup>1)</sup>The idea of the potential field of the "extra" particle as an external perturbation for the system of particles was first introduced and used in<sup>[29]</sup> for the study of the functions  $F_s$ .

where  $\chi(\mathbf{r})$  is defined by

$$\chi(\mathbf{r}) = e^{-\Phi(\mathbf{r})/kT} - 1.$$

Substitution of the series (26) and (27) in (24) under the assumption that the function  $f(u, v)$  does not depend explicitly on  $n$  leads, in zeroth order in  $n$ , to the condition

$$f(1 + \chi(\mathbf{r}), \Phi(\mathbf{r})) - f(1, 0) = \left. \frac{\partial f}{\partial u} - kT \frac{\partial f}{\partial v} \right|_{u=1, v=0} \chi(\mathbf{r}) \quad (28)$$

and in first order in  $n$  to the condition

$$\left. \frac{\partial f}{\partial u} \right|_{u=1+\chi(\mathbf{r}), v=\Phi(\mathbf{r})} - \left. \frac{\partial f}{\partial u} \right|_{u=1, v=0} [1 + \chi(\mathbf{r})] = -kT \left. \frac{\partial f}{\partial v} \right|_{u=1, v=0} \chi(\mathbf{r}). \quad (29)$$

Satisfaction of the first condition (28) guarantees the correct value of the second virial coefficient for the gas pressure and correct contributions of order  $n^2$  for all the thermodynamic functions. Analogously, satisfaction of the condition (29) guarantees a correct third virial coefficient for the pressure and correct contributions of order  $n^3$  to all the thermodynamic functions of the gas. It is possible to continue in this manner the list of requirements on the function  $f(u, v)$  and obtain continuously improving results for the function  $g(\mathbf{r})$  and for the thermodynamic functions expanded in powers of the density. However, if we are interested in describing the properties of a liquid and not of a moderately dense gas, such an approach is not the best. It is quite possible and permissible to use approximations that provide good results for a liquid or a strongly compressed gas but do not lead to exact values of, say, the fourth or fifth virial coefficient. A likely estimate of the total sum of all the terms of the virial series is more important than a correct description of a small number of the initial terms of the series. This does not pertain, however, to the very first terms of the series, which must be estimated accurately to be able to extrapolate the results of the theory to the case  $n \rightarrow 0$ . The conditions (28) and (29) must therefore be preserved.

It is difficult to indicate other general requirements imposed a priori on the function  $f(u, v)$  in (24) and expressible in terms connected with the function  $f(u, v)$  itself. The degree of suitability of different assumptions concerning the function  $f(u, v)$  must therefore be assessed from results of the calculations of the function  $g(\mathbf{r})$  and of the thermodynamic properties of the system. By now, two relatively simple approximations have been thoroughly studied: the initial Percus approximation, corresponding to the choice of the function  $f(u, v)$  in the form

$$f(u, v) = ue^{v/kT}, \quad (30)$$

and the approximation of the hyper-netted chains (HNC), corresponding to the choice

$$f(u, v) = \ln u + (v/kT). \quad (31)$$

It can be verified that both forms of  $f(u, v)$  given by (30) and (31) satisfy the conditions (28) and (29).

The form of the functions  $C(\mathbf{r})$ , which follows from equation (24) in the approximations (30) and (31), was given in Eqs. (10) and (11) above. Together with Eq. (9), this leads to the integral PY equation for  $g(\mathbf{r})$

$$g(\mathbf{r}) e^{\Phi(\mathbf{r})/kT} = 1 + n \int [g(\mathbf{r} - \mathbf{r}') - 1] g(\mathbf{r}') [1 - e^{\Phi(\mathbf{r}')/kT}] d\mathbf{r}' \quad (32)$$

and to the equation of the hyper-netted chains

$$g(r) + [\Phi(r)/kT] = -n \int [g(r-r') - 1] \{g(r') - 1 - \ln g(r') - [\Phi(r')/kT]\} d^3r' \quad (33)$$

Obviously, the first of them is particularly simple, even simpler than the KB equations (7) and (8). It is interesting that the latter can also be obtained from a general approximation scheme of the Percus type, if one chooses in (21) a certain functional  $\Pi\{\psi\}$  and accordingly a certain function  $f(u, v)$  equal to<sup>[28]</sup>

$$f(u, v) = -u\nabla v,$$

and if one modifies very slightly the subsequent calculations.

Equations (32) and (33) as well as their corollaries have been well investigated. It turns out that in the region of the liquid state proper, the PY equation (32) is not inferior in the quality of the results to the seemingly more accurate (33). The results of the corresponding calculations are given and discussed in Chap. 3 of the review.

A general shortcoming of all the simple approximations for the function  $f(u, v)$  follows from their insufficient accuracy and is the inconsistency in the result of calculations of the thermodynamic characteristics of the system from Eqs. (1)–(3). The general requirement that Eqs. (1) and (3) be mutually consistent is expressed in terms of higher-order distribution functions, and therefore cannot be expressed as a requirement imposed on the function  $f(u, v)$ . The quality of the results can be improved in part even for very simple functions  $f(u, v)$ , if the expansion (21) is not confined to the linear approximation. Allowance for the next higher terms of the expansion in the PY equations and in the HNC equations leads to better results, but the equations themselves become very complicated. The correction terms in both equations include a three-body distribution function, and the integral equation for  $g(r)$  cannot be solved in this approximation without making use of approximations for  $F_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ . In case there are likewise no unambiguous prescriptions, and it was proposed to use the method of functional expansion also to approximate  $F_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$  in the correction terms<sup>[28]</sup>. In the so-called PY-2 equation, one expands the functional

$$F_2(\mathbf{r}_1, \mathbf{r}_2 | \psi) \exp\{(kT)^{-1} [\psi(\mathbf{r}_1) + \psi(\mathbf{r}_2)]\}. \quad (34)$$

If, as before,  $\psi(\mathbf{r})$  is regarded as the field of the particle added to the system and two terms of the expansion are retained, one can obtain an expression for the three-body distribution function in terms of the RDF. In the derivation of equations PY-II and HNC-II one expands the functional

$$F_2(\mathbf{r}_1, \mathbf{r}_2 | \psi) / F_1(\mathbf{r}_1 | \psi) F_1(\mathbf{r}_2 | \psi).$$

Analogously, in the derivation of equation SEN-II, the expanded functional is the logarithm of the function (34). Finally, mention should be made of a paper<sup>[31]</sup> in which the higher approximations were also considered, but on the basis of diagram expansions. It is possible to obtain in this manner the equations PY-II' and HNC-II', which differ somewhat from equations PY-II and HNC-II, and also the next higher approximations in density, which lead to the equations PY-III and HNC-III.

The described method of expansion in functional series makes it possible to obtain higher approximations to the equations of the PY type and can be used to

obtain equations for the pair distribution functions of systems situated in external fields (electric, gravitational, etc.)<sup>[32]</sup>, and also in the case when the interparticle interaction is non-central<sup>[33]</sup>. In the presence of an external field, the problem of integrating the PY equations becomes more complicated, for the homogeneity of the single-particle distribution is then violated. In this case it is necessary to have one more relation, other than the PY equation, between the single-particle and two-particle distribution functions. Such an equation can be the first equation of the Bogolyubov chain of equations, and the latter together with the PY equation comprises a closed system for the determination of  $F_1(\mathbf{r}_1)$  and  $F_2(\mathbf{r}_1, \mathbf{r}_2)$ .

c) Analytic solution of the Percus-Yevick equation for a system of hard spheres. Even though numerical calculations based on the PY equation are quite numerous and extensive, and were made for almost all densities starting with rarefied gases and ending with states close to the triple point, the analytic properties of this equation have been very little studied. Only most recently has it become possible to show that the PY equation, under definite but very general conditions imposed on the interparticle potential, has a solution analytic in the density near  $n = 0$ ; this solution is unique for density values not exceeding a certain maximum. The solution remains analytic and unique also for the HNC equation. An analytic solution in explicit form was obtained, on the basis of the PY equation<sup>[35,36]2)</sup>, only for the case of a model system consisting of hard spheres. A hard-sphere system is a convenient model for the study of the behavior of dense gases and liquids, and recently interest in this model has increased because of the successful application of perturbation theory to classical liquids<sup>[38,39]</sup>. Back in 1954, Zwanzig<sup>[40]</sup> proposed to consider the attraction forces in liquids as perturbations to a hard-core potential and developed on this basis a perturbation theory for classical liquids. The theory remained unused for a long time, however, because of the lack of a sufficiently good zeroth approximation. Now, following the work by Barker and Henderson<sup>[38,39]</sup>, it has become obvious that the hard-sphere system is a very good zeroth approximation for a real liquid. Therefore the analytic PC solution for a hard-sphere system is not merely of pure academic interest, but is of great applied significance, since it provides an exact zeroth approximation for a real liquid. We present here the solution obtained in<sup>[35,36]</sup> for the PY equation.

We put

$$\tau(r) = re^{\Phi(r)/kT} g(r).$$

Substituting in (32) the hard-sphere potential for  $\Phi(\mathbf{r})$  and introducing bipolar coordinates, we obtain after integrating with respect to the angle variable

$$\tau_n(x) = \tau(x) \quad n < x < n+1 \quad (n = 0, 1, 2, \dots) \quad (35)$$

<sup>2)</sup> There is one more known exact analytic solution of the PY equation for a hard-core potential with square well, under the condition that one considers the limit of infinitesimally narrow and infinitesimally deep well (hard sphere with surface adhesion)<sup>[37]</sup>. This solution is based in final analysis, however, on a solution of the hard-sphere problem, and will not be considered here.

where  $x = r/D$  is the dimensionless length ( $D$  is the diameter of the hard sphere) and  $H(t)$  is the Heaviside function. It can be verified directly from (35) that the fourth and higher derivatives of  $\tau(x)$  are discontinuous at  $x = 1$ , while the second and higher derivatives are discontinuous at  $x = 2$ . These discontinuities give rise in turn to discontinuities of the higher-order derivatives at  $x = 3, 4$ , etc. It is therefore natural to seek a piecewise-analytic solution of (35) with derivatives that are discontinuous at  $x = 1, 2, 3, \dots$ . We define the functions  $\tau_n(x)$  by the equations

$$\tau(x) = \left(1 + 4\pi n D^3 \int_0^1 s \tau(s) ds\right) x - 2\pi n D^3 \int_0^1 \tau(s) \left[ \int_{|x-s|}^{x+s} H(t-1) \tau(t) dt \right] ds, \tag{36}$$

Taking the Laplace transform of (35) and using the definition (36), we obtain

$$\sum_{n=1}^{\infty} \int_n^{n+1} \tau_n(s) e^{-\lambda s} ds = \left\{ \lambda^{-2} \left[ 1 + 24\eta \int_0^1 \tau_0(s) s ds \right] - \int_0^1 \tau_0(s) e^{-\lambda s} ds \right\} \left[ 1 + 24\eta \lambda^{-1} \int_0^1 \tau_0(s) \text{sh}(\lambda s) ds \right]^{-1}, \tag{37}$$

where  $\eta = \pi D^3 n / 6$  is the dimensionless density. On the basis of (37) we can establish a set of sufficient conditions imposed on the function  $\tau_0(x)$ , such that  $\tau(x)$  is a piecewise-analytic function. To this end we transform (37) by successive integrations by part into

$$e^{-\lambda} \sum_{l=0}^{\infty} [\tau_0^{(l)}(1) / \lambda^{l+1}] + \sum_{n=2}^{\infty} e^{-n\lambda} \sum_{l=0}^{\infty} \lambda^{-l+1} [\tau_n^{(l)}(n) - \tau_{n-1}^{(l)}(n)] = e^{-\lambda} (\alpha + \beta e^{-\lambda}) / (\gamma e^{-2\lambda} + \delta e^{-\lambda} + \epsilon), \tag{38}$$

where

$$\left. \begin{aligned} \alpha &= \lambda^{-2} \left[ 1 + 24\eta \int_0^1 s \tau_0(s) ds \right] - \sum_{l=0}^{\infty} [\tau_0^{(l)}(0) / \lambda^{l+1}], \\ \beta &= \sum_{l=0}^{\infty} [\tau_0^{(l)}(1) / \lambda^{l+1}], \quad \gamma = 12\eta \lambda^{-1} \sum_{l=0}^{\infty} [\tau_0^{(l)}(1) / \lambda^{l+1}], \\ \delta &= 1 - 24\eta \lambda^{-1} \sum_{l=0}^{\infty} [\tau_0^{(2l)}(0) / \lambda^{2l+1}], \\ \epsilon &= 12\eta \lambda^{-1} \sum_{l=0}^{\infty} [(-1)^l \tau_0^{(l)}(1) / \lambda^{l+1}] \end{aligned} \right\} \tag{39}$$

(the superscript of  $\tau_0$  indicates the order of the derivative). If we expand the right-hand side of (38) in powers of  $e^{-\lambda}$  and equate the corresponding coefficients in the left and right hand sides of (38), we can find the limitations imposed on the derivatives of the function  $\tau_0(x)$  at the points  $x = 0$  and  $x = 1$ . This procedure leads to very cumbersome formulas, and we shall not write out here the corresponding relations. Instead, we can use the fact that if  $\alpha + \beta e^{-\lambda}$  is a factor of  $\gamma e^{-2\lambda} + \delta e^{-\lambda} + \epsilon$ , then all these limitations can be shown to be automatically satisfied. The condition for division without a remainder is

$$\alpha (\delta - \alpha \gamma \beta^{-1}) = \epsilon \beta.$$

Substituting here formulas (39) and equating like powers of  $\lambda^{-1}$ , we obtain

$$\tau_0^{(0)}(0) = 0, \quad \tau_0^{(1)}(0) = 1 + 24\eta \int_0^1 s \tau_0(s) ds, \quad \tau_0^{(2)}(0) = -12\eta [\tau_0^{(0)}(1)]^2, \dots$$

These equations determine uniquely the function  $\tau_0(x)$  and lead to the result

$$\tau_0(x) = ax + bx^2 + cx^4, \tag{40}$$

where

$$a = (2\eta + 1)^2 / (\eta - 1)^4, \quad b = -3\eta (2 + \eta)^2 / 2 (\eta - 1)^4, \\ c = \eta (2\eta + 1)^2 / 2 (\eta - 1)^4.$$

Knowing the function  $\tau_0(x)$  we can obtain the equation of state. Substitution of (40) in (1) and (3) leads respectively to the equations

$$(p/nkT)_{\text{vir}} = (1 + 2\eta + 3\eta^2) / (1 - \eta)^2, \tag{41}$$

$$(p/nkT)_{\text{comp}} = (1 + \eta + \eta^2) / (1 - \eta)^3 \tag{42}$$

(the pole of the pressure at  $\eta = 1$  corresponds to a physically unattainable state, since  $\eta < 1$  even for the closest packing).

It follows from the obtained equations of state that the pressure predicted by the PY theory is higher than the pressure of an ideal gas (it is higher by one order of magnitude for a dense system at  $\eta \sim 0.5$ ). In a liquid, however, the pressure is known to be much less than in a gas at the same temperature. Therefore the model system of hard spheres accounts poorly for the "liquid" pressures in the PY theory. It can also be seen that the two equations of state are equal to each other to order  $\eta^2$  inclusive. The difference between them becomes negligibly small in comparison with the principal term at

$$3\eta^3 \ll \eta^2 + \eta + 1.$$

Figure 1 shows plots of the equation of state for a hard-sphere system in accordance with the PY equation, and for comparison the results of calculations by the BBGKY (Bogolyubov-Barker-Green-Kirkwood-Yvon) equation, the HNC equation, and the MD equation (central solid curve) ([41], p. 85). It can be seen that the BBGKY theory gives the worst result, whereas the best agreement with the computer experiment is obtained with the PY equation in conjunction with the compressibility equation. It is interesting that the curves calculated from Eqs. (41) and (42) are on opposite sides of the liquid branch obtained in the computer experiment. Certain workers therefore prefer to use not the virial equation (VE) or the compressibility equation (CE) as the equation of state of the hard spheres, but a certain combination of the two. For example, fair agreement with the MD results is obtained by the simple arithmetic mean of these equations [42]. On the other hand, if the equation of state is written in the form [43]

$$p/(nkT) = (1 + \eta + \eta^2 - \eta^3) / (1 - \eta)^3$$

(which differs from the arithmetic mean in that  $\eta^3$  in the numerator is preceded by 1 instead of 1.5), then this equation is in better agreement with the computer calculations for hard spheres than the Pade approximation of Ree and Hoover [6].

From the known function  $\tau_0(x)$  it is easy to determine the direct correlation function in the Percus approximation. From relation (10) we obtain for a system of hard spheres, with allowance for the definition of the function  $\tau(x)$ ,

$$C(x) = \begin{cases} -(a + bx + cx^2), & x < 1, \\ 0, & x > 1. \end{cases} \tag{43}$$

The direct correlation function is "short-range," as is proposed in any theory using  $C(x)$ . Although the direct

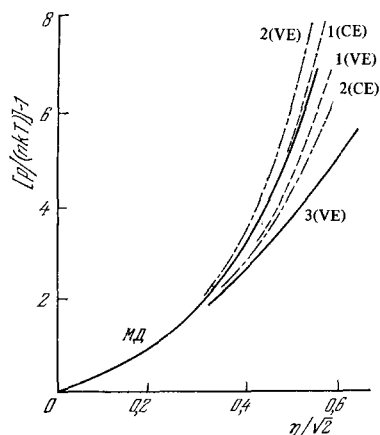


FIG. 1. Equations of state for a system of hard spheres in accordance with PY (1), HCN (2), and BBGKY (3), obtained using the virial equation and the compressibility equation.

correlation function has no immediate physical meaning, knowledge of this function makes it possible to determine the most important characteristic of the correlation structure of the system, namely its structure factor. By definition, the structure factor of  $S(\mathbf{k})$  is given by

$$S(k) = 1 + n \int [g(r) - 1] e^{-ikr} dr.$$

If we take the Fourier transform of (10), we can express the Fourier transform of the RDF in terms of the Fourier transform of the direct correlation function, obtaining for the hard-sphere system

$$S(kD) = [1 - nC(kD)]^{-1}, \quad (44)$$

where

$$C(kD) = -4\pi D^3 \int_0^1 s^2 [\sin(skD)/skD] (a + bs + cs^3) ds. \quad (45)$$

Although the direct correlation function for real liquids does not terminate as abruptly as (43) (cf. (25)), the use of the solution for hard spheres as an approximation in the calculation of the structure factor leads to satisfactory agreement with the experimental data. Ashcroft<sup>[44]</sup> used the solution (44)–(45) to calculate the structure factors of noble gases, using the sphere diameter  $D$  as the parameter.

Figure 2a shows a typical plot of  $S(k)$  for Ar and the curves obtained from the experiments of Aisenstein and Gingrich<sup>[45]</sup>, corresponding to the temperatures 84.4 (1–2) and 144.1° K (3–4) and densities 1.407 and 0.87 g/cm<sup>3</sup>, respectively. Good agreement at both densities is obtained with  $D = 3.44$  Å. The data of Gingrich and Tompson, taken near the triple point, are also well described near the principal peak (at  $D = 3.46$  Å).

The RDF for a system of hard spheres can be obtained by substituting  $\tau_0(x)$  in (37). By obtaining the Laplace transform of the function  $\tau(x)$  in this manner, we obtain the distribution function itself by taking the inverse transform. The distribution function has a very complicated analytic form, and we confine ourselves here only to a plot of  $g(r)$  (Fig. 2b) based on the data of<sup>[47,48]</sup>, referring the reader to<sup>[35,47-49]</sup> for details.

The analytic expression obtained from the PY equation for the RDF is usually assumed in practical calcu-

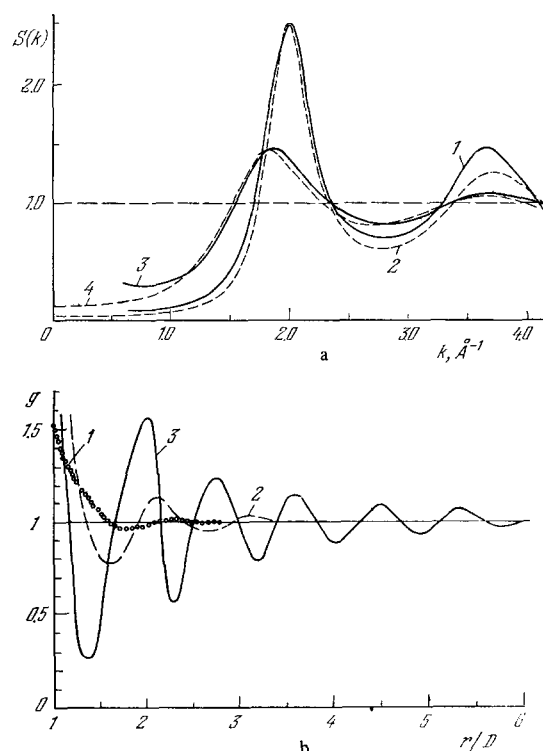


FIG. 2. a) Dependence of structure factor  $S$  on  $k$  for Ar (solid curves—from experiment on x-ray diffraction, dashed—from PY equation) for hard spheres with  $D = 3.44$  Å<sup>[44]</sup>; b) RDF for a system of hard spheres in accordance with the PY equation at densities  $nD^3 = 0.3$  (1), 0.7 (2), and 1.1 (3).

lations of the properties of a system of hard spheres to be exact, in spite of the approximate character of the PY equation. If we go beyond the framework of the PY approximation, then we can obtain improved values of the RDF by introducing a phenomenological correction term in the analytic solution of the PY equation. It is usually chosen such that the compressibility and virial equations become self-consistent<sup>[50]</sup>.

### 3. RESULTS OF NUMERICAL CALCULATIONS BY THE INTEGRAL-EQUATION METHOD

a) Calculations of the RDF and of the thermodynamic characteristics. The solution of the integral equations for the RDF depends strongly on the form of the interparticle interaction potential. Since at the present time we do not know the exact form of the potential for liquids, it becomes necessary to use model potentials in the solution of the integral equations. To estimate the correctness of the results it is necessary to know the accuracy of the corresponding integral equations. The methods used to verify the correctness of the integral equations for the RDF can be broken up into two groups:

1) Calculations based on simple potential functions, wherein the obtained equations of state (virial coefficients) are compared with the exact theoretical values or, in the case of more complicated potentials, with the data of the MC or the MD methods.

2) More realistic potentials (for example, of the Lennard-Jones type) are used and the results are verified by comparison with relevant experimental data.



Table I

VC number	Calculation method	Rods	Squares	Cubes	Spheres
4th	Exact	1	3.667	11.333	0.2869
	PY	1	3.778	12.289	0.2969
	PY-2	1	3.667	11.333	0.2869
5th	Exact	1	3.7222	3.1597	0.1097
	PY	1	4.2361	12.4303	0.121
	PY-2	1	3.639	1.701	0.107
	PY-II'	1	3.7222	3.2431	0.1098
6th	Exact	1	3.02500	-18.8796	0.0386
	PY	1	4.42000	9.2067	0.0449
	PY-2	1	3.020	-21.203	—
	PY-II'	1	3.11204	-13.5939	—
	PY-III	1	3.02500	-18.8777	—

Table II

VC number	Calculation method	Rod	Squares	Cubes	Spheres
4th	Exact	1	3.667	11.333	0.2869
	HNC	0.9167	2.944	6.639	0.2092
	HNC-2	1	3.667	11.333	0.2869
5th	Exact	1	3.7222	3.1597	0.1097
	HNC	0.800	1.8042	-6.9394	0.049
	HNC-2	1.0833	4.039	5.198	0.122
	HNC-II'	1	3.6656	2.0301	0.1065
6th	Exact	1	3.02500	-18.8796	0.0386
	HNC	0.70278	0.96500	-2.2133	0.0281
	HNC-II	1	2.94468	-16.9473	—
	HNC-III	1	3.00926	+19.0401	—

Table III

n*	Pade approximation	PY-II and VE	PY and VE	PY and CE	HNC and VE	HNC and CE
0.354	2.24	2.24	2.22	2.25	2.32	2.19
0.573	3.99	4.02	3.81	4.05	4.39	3.65
0.668	5.25	5.22	4.89	5.36	5.94	4.59

Table IV

n*	Pade approximation	PY-II and VE	PY and VE	PY and CE	HNC and VE	HNC and CE
0.354	4.22	4.27	4.03	4.26	4.54	3.96
0.573	10.50	10.1	9.41	10.66	12.51	8.60
0.668	16.35	15.7	13.56	16.18	18.54	12.00

The first group of methods has the advantage that the equations can be rigorously verified (although the result may not describe the behavior of real liquids). In the second group, any conclusions concerning the applicability of the discussed equations become indefinite to a certain degree, owing to the inaccuracy of the potential function used in the calculations. It is therefore preferable to use methods of the first group, all the more since the most recent developments of computer technology make it possible to perform computer experiments with sufficiently complicated forms of the interparticle potential. By now, many computer calculations were made to obtain the equations of state and RDF of different systems: one-, two-, and three-dimensional spheres, particles with Lennard-Jones interaction, etc. Apart from the statistical errors inherent in calculations with a relatively small number of particles and a finite calculation time, computer experiments yield exact results for a specified potential.

The perturbations introduced in real systems by many-particle forces and by inexact knowledge of the form of the potential do not appear in computer calculations. Therefore data obtained with a computer experiment can serve as a criterion for the validity of any theory used to calculate thermodynamic characteristics or RDF.

Let us examine the results of numerical integration for the simplest forms of the interparticle potential. Verlet<sup>[28]</sup> used the PY and HNC equations for model one-, two-, and three-dimensional gases of hard rods, squares, and cubes. Six virial coefficients (VC) were calculated from the PY and PY-2 equations and five coefficients in the case of the HNC and HNC-2 equations. These results can be supplemented with calculations of a fifth VC by means of equations PY-II' and HNC-II', and of a sixth VC by equations PY-III and HNC-III<sup>[31]</sup>. The results of<sup>[28]</sup> and<sup>[31]</sup> and of analogous calculations for a system of hard spheres<sup>[51-53]</sup> are compared with the exact results in Table I (on the basis of the PY equations) and Table II (on the basis of the SEN equation).

As seen from the tables, the PY equation gives the correct values of the fourth, fifth, and sixth VC for gases of hard rods. This is due to the fact that the PY equation is exact for this case<sup>[25]</sup>. In the remaining cases, there is no such agreement, and the discrepancy with the exact values increases with increasing number of the VC. However, even in the next approximation, on the basis of equations PY-2 and HNC-2, four virial coefficients turn out to be exact. The use of the HNC-2 equation improves somewhat the agreement between the calculations of the fifth VC with the exact ones, but one can see that the PY approximation gives better results. In the PY-2 approximation, the sixth VC differs from the exact one for a system of hard squares only in the fourth decimal place, and is somewhat less accurate for hard cubes. The best agreement between the theory and the exact values is obtained in the PY-III theory: the sixth VC for both hard cubes and hard squares practically coincide with the exact values.

It is interesting to compare the other thermodynamic characteristics of the simplest model systems with those calculated by the PY equation. For the system of hard spheres there are reliable data from three sources: MD<sup>[54]</sup>, MC-method calculations<sup>[55-57]</sup>, and the seven-term virial expansion with the Pade approximation<sup>[6]</sup>. These three methods lead to identical results in the liquid-state region, and can be regarded as accurate. Table III compares the values of the compressibility factors  $p/nkT$ , obtained using the VE (1) on the basis of the PY-2 equation, with the exact values obtained from an analytic solution of the PY equations (41) and (42) and from the HNC equation<sup>[58]</sup> with numerical calculations<sup>[59-62]</sup>. A similar comparison is given in Table IV<sup>[58]</sup> for the reciprocal compressibility  $(kT)^{-1}(\partial p/\partial n)_T$ .

As seen from these tables, the PY-2 equation agrees satisfactorily with the exact values and is much better than the PY equation and the HNC at high densities, while the PY equation is better than the HNC.

Figure 3 shows plots of the RDF for a system of hard spheres. The PY equation leads to the largest deviation of the RDF from the exact value, and the

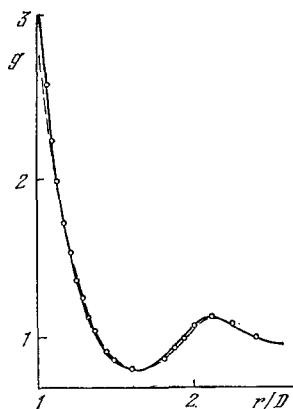


FIG. 3. RDF for a system of hard spheres at  $nD^3 = 0.068$ . The dashed and solid curves were calculated from the PY and PY-II equations, and the circles are the result of MC calculations [62].

PY-II equation yields a curve that almost coincides with the exact one.

It is seen from the presented results of the numerical integration of the PY equation and HNC that the use of the virial equation (1) or the compressibility equation (3) to calculate the thermodynamic characteristics leads to different values, with differences that are sometimes quite appreciable. Many authors have therefore proposed "self-consistent" theories by introducing into the PY equation or the HNC a phenomenological parameter chosen to reconcile the virial coefficients calculated in accordance with the VE or the CE<sup>[63-70]</sup>. All these theories are based in one way or another on replacing the PY expression (10) for  $C(r)$  by other expressions with indeterminate parameters. For example, Rowlinson<sup>[65]</sup> started with the expression

$$C(r) = g(r) (1 - e^{\Phi(r)/kT}) + \mu [g(r) - 1 - \ln(g(r) e^{\Phi(r)/kT})]. \quad (46)$$

It is obvious that this yields the Percus approximation at  $\mu = 0$  and the HNC equation at  $\mu = 1$ . If  $\mu$  is assumed to be a function of the density and the temperature, it is possible to obtain agreement between the VC calculated by the VE and the CE.

A diagram analysis carried out by Morita<sup>[70]</sup> has shown why it is reasonable to choose the structure of the self-consistent approximations in the form (46). If we analyze the structure of the diagrams summed in the PY and HNC approximations, it turns out that for each diagram  $\Gamma_1$  taken into account in the HNC theory but neglected in the PY theory it is possible to find several diagrams  $\Gamma_2$  among those discarded in the HNC approximation, such that the diagrams  $\Gamma_2$  partially cancel the contribution of the diagrams  $\Gamma_1$ . However, since the cancellation is nevertheless incomplete, the diagrams  $\Gamma_1$  can be included in the calculation but with a certain weight. The parameter in (46) does indeed play the role of such a weighting factor.

We proceed now to calculations with the more realistic Lennard-Jones (LJ) potential

$$\Phi(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6].$$

Figure 4 shows the isotherms  $T^* = 2.74$  (the temperature is expressed in units of  $\epsilon/k$ ) obtained on the basis of different theories of RDF and from two possible equations of state (VE and CE). As seen from the diagrams, at such relatively high temperatures the PY equation gives good agreement with the exact results.

Let us examine now the critical region. Table V lists

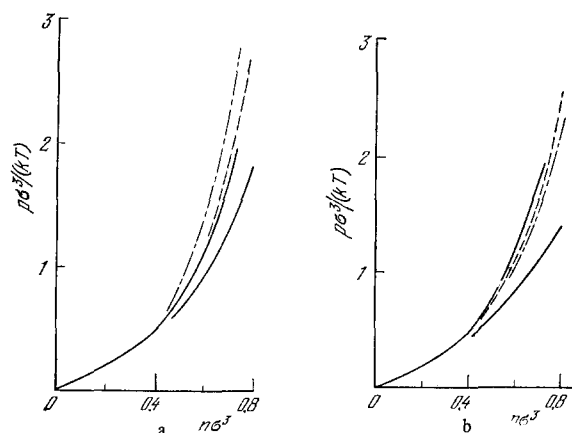


FIG. 4. Equation of state by the PY theory with LJ potential (isotherm  $T^* = 2.74$ ) using the VE (a) and the CE (b). The upper solid curves were calculated by the MD method [71], the lower ones by the BBGKY theory, and the dash-dot and dashed curves were calculated by the HNC and PY theories, respectively.

the critical constants (in dimensionless units) calculated on the basis of different integral equations with LJ potential<sup>[71]</sup>. An analysis of these data shows that here, too, the PY equation is better than the HNC or BBGKY equation. In this temperature region, the BBGKY equation gives very poor critical constants; although the PY and HNC theories are inaccurate, the discrepancy is relatively small, on the order of 10%.

Let us examine, finally, the region of low temperatures. In this region, both the PY equation and the SEN equation give much worse results<sup>[48,72]</sup>. The thermodynamic properties of a system with LJ potential, calculated by the PY equation, are compared in Table VI with the MD data ( $T^*$  and  $n^*$  are the dimensionless temperature and particle-number density, and  $E_i$  is the internal energy)<sup>[47]</sup>. It follows from this table that the PY equation gives incorrect values of the pressure in the liquid phase, regardless of whether the VE or the CE is used. Both values of the pressure differ from the exact ones by more than 100%. It is interesting to note, however, that the exact values lie again between those calculated by the PY method, and in those cases when  $p_{\text{comp}}$  is not negative, the simple arithmetic mean deviates from the exact value by only 10%.

The pressure is very sensitive to even small errors in the RDF. In this respect, the internal energy is a more "favorable" function. We defer the discussion of the fact to Sec. C.

Let us examine the results of the RDF calculation for systems with LJ potentials at different temperatures. Broyles and co-workers<sup>[73]</sup> investigated the high-temperature isotherm  $T^* = 2.74$  at different densities up to  $n^* = 10/9$ , on the basis of the BBGKY, PY, and HNC theories. The best agreement with the RDF by the MC method is obtained from the PY equation. The BBGKY equation leads to the worse results, especially at high densities (Fig. 5).

At low temperatures, as seen from Fig. 5b, the RDF calculated from the PY equation differs significantly from the exact one. The first RDF peak obtained by the PY method is somewhat broader and higher than that obtained by the MD method, and the maxima and minima are shifted somewhat towards lower distances. On the

Table V

Calculation method	$T_{cr}^*$	$n_{cr}^*$	$p_{cr}^*/n_{cr}^*kT_{cr}^*$	Equation of state
BBGKY	$1.45 \pm 0.03$	$0.40 \pm 0.05$	$0.44 \pm 0.04$	VE
BBGKY	$1.58 \pm 0.02$	$0.40 \pm 0.03$	$0.48 \pm 0.03$	GE
HNC	$1.25 \pm 0.02$	$0.26 \pm 0.03$	$0.35 \pm 0.03$	VE
HNC	$1.39 \pm 0.02$	$0.28 \pm 0.03$	$0.38 \pm 0.04$	CE
PY	$1.25 \pm 0.02$	$0.29 \pm 0.03$	$0.30 \pm 0.02$	VE
PY	$1.32 \pm 0.02$	$0.28 \pm 0.03$	$0.36 \pm 0.02$	CE
PY-II	$1.36 \pm 0.04$	$0.35 \pm 0.03$	$0.31 \pm 0.03$	VE
PH-II	$1.33 \pm 0.03$	$0.33 \pm 0.04$	$0.34 \pm 0.03$	CE
MD	$1.32-1.36$	$0.32-0.36$	$0.30-0.36$	—
Experimental for Ar	1.26	0.316	0.297	—

Table VI

$T^*$	$n^*$	$(p/nkT)_{comp}$	$(p/nkT)_{MD}$	$(p/nkT)_{vir}$	$E_i/NkT$	
					MD	PY
0.719	0.85	-0.60	0.36	2.82	-8.51	-8.28
0.796	0.85	-0.10	0.99	2.97	-7.70	-7.51
0.880	0.85	0.54	1.64	3.17	-6.75	-6.61
1.128	0.85	1.71	2.78	3.52	-5.05	-4.98

whole, however, the agreement is quite satisfactory.

Thus the data of the PY theory below the critical point should be used with great caution when the pressure is calculated from the RDF, whereas the energy is obtained from the RDF with sufficient accuracy.

So far we have considered the results of numerical integration of the equations for the RDF in comparison with the exact data. It is of interest to investigate the applicability of the PY and HNC theories to real systems, primarily noble gases. A detailed investigation of this question was carried out by Throop and Bearman<sup>[74]</sup>. They calculated with the aid of the PY equation the thermodynamic functions and the RDF for the temperatures and densities near the coexistence curve. The comparison was made with the experimental data on Xe and Ar<sup>[75]</sup> and with analogous calculations by the HNC equations<sup>[76]</sup>. Near the coexistence curve, for the isotherm  $T^* = 1.5$  up to  $n^* = 0.3$ , the pressures calculated by the HNC theory with the VE are closer to the experimental values of the pressure for Xe and Ar than those obtained by the PY theory, but the difference between the two theories is extremely small (less than 0.5%). For larger densities,  $n^* \geq 0.3$ , the PY theory is better. At  $n^* = 0.6$  the pressure according to PY is 29% higher than the experimental pressure for Ar and 49% higher according to the HNC theory. In calculations with the VE, the qualitative conclusions remain the same as before, but at densities  $n^* \geq 0.3$  the agreement between the theoretical and experimental values for Xe is much less satisfactory than for Ar, namely, at  $n^* = 0.6$  the HNC and PY pressures exceed the experimental values by 100 and 75%, respectively. Both the difference between the results of the PY and HNC theories and the difference between these theories and experiment increase with increasing density (Fig. 6a). As seen from the figure, the intrinsic inconsistency of the PY theory at this temperature is much less than in the HNC theory, and the inconsistencies in both theories increase with increasing density. As to the internal energy, it is practically the same in both theories, and the curves practically coincide. This is valid also with respect to the entropy. The deviation of these thermodynamic quantities from experiment increases with density and is of the order of fractions of 1%.

We now compare the results of the calculations for different temperatures. It turns out that for Ar at all the temperatures considered in<sup>[74]</sup> ( $T^* = 1.4, 1.89,$  and  $3.57$ ) the experimental equation of state lies between  $p_{comp}$  and  $p_{vir}$ , and with increasing temperature the agreement between the results with the VE and CE improves. At  $n^* = 0.6$ , the difference between  $p_{comp}$  and  $p_{vir}$  is 48% at  $T^* = 1.4$ , 18% at  $T^* = 1.89$ , and 4% at

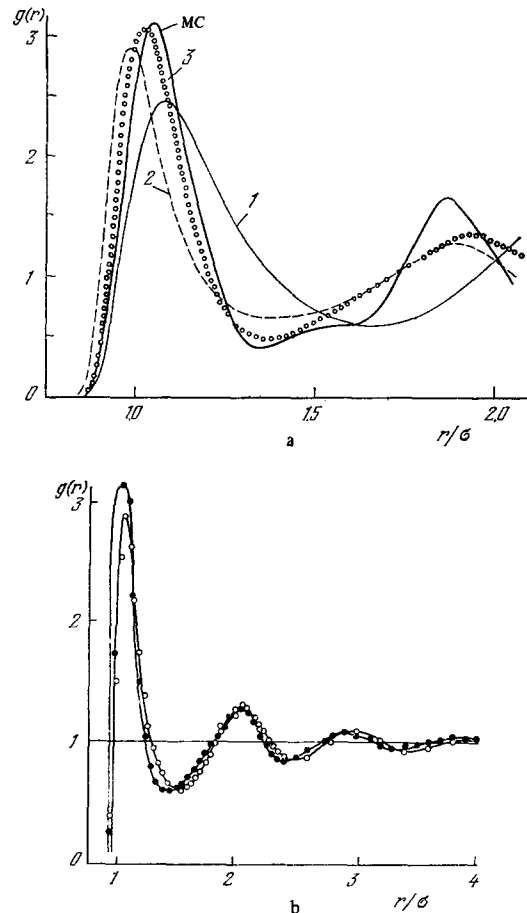


FIG. 5. The RDF as a function of the distance: a) for a density  $n^* = 10/9$  and a temperature  $T^* = 2.74$  on the basis of the equations of PY (1), HNC (2), BBGKY (3) with LJ potential (thick curve—by the MC method)<sup>[73]</sup>, b) calculated from the PY equation (dark circles; light circles—MD calculations,  $T^* = 0.88$ ,  $n^* = 0.85$ )<sup>[48]</sup>.

$T^* = 3.57$ . For much higher temperatures, the virial and compressibility isotherms almost coincide, differing by 0.5% at  $n^* = 0.6$ .

In the comparison of the theoretical calculations with the experimental results, attention was called to the following circumstance. The agreement with experiment is very sensitive to the choice of the parameters of the LJ potential. For example, the value of  $p/nkT$  obtained at  $T^* = 1.3$ ,  $n^* = 0.6$ , and  $\epsilon/k = 119.3^\circ\text{K}$  and  $\sigma = 3.43 \text{ \AA}$  differs by 11% from the value obtained when the parameters  $\epsilon/k = 119.8^\circ\text{K}$  and  $\sigma = 0.3.405 \text{ \AA}$  are used. Therefore the seeming satisfactory agreement between theory and experiment for Ar and the less satisfactory agreement with the data on Xe may be due to a certain leeway in the choice of the parameters, or else to the fact that the LJ potential may not be applicable to Xe.

We present also the results of calculations by

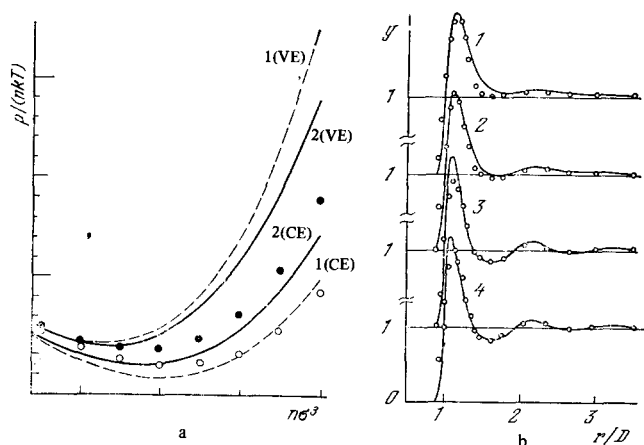


FIG. 6. a) Equation of state (isotherm  $T^* = 1.4$ ) for a system with LJ potential on the basis of the PY and HNC equations (dark circles—experimental points for Ar, light—for Xe: 1—HNC, 2—PY) [74]; b) the RDF obtained from the PY equation with LJ potential (solid curves—PY equation, circles—experimental results [77] for Ar: 1— $T^* = 1.361$ ,  $n^* = 0.167$ ; 2— $T^* = 1.319$ ,  $n^* = 0.319$ ; 3— $T^* = 1.194$ ,  $n^* = 0.541$  and 4— $T^* = 1.277$ ,  $n^* = 0.541$ ).

Watts [77] with an LJ potential. Figure 6b shows plots of the RDF for four states that differ in density and temperature, compared with the experimental results for Ar ( $\epsilon/k = 119.8^\circ\text{K}$ ,  $\sigma = 3.405 \text{ \AA}$ ). An analysis of the plots shows that the agreement between theory and experiment is satisfactory. It is interesting that it is better at high densities.

The  $p^*/kT^*$  data in Table VII show that the LJ potential accounts satisfactorily for the thermodynamic properties of argon in the PY approximation in a sufficiently wide range of temperatures and densities when the VE is used [77].

b) Determination of the interparticle potential. So far, we have assumed that the potential is given and we have assessed the accuracy and validity of the corresponding integral equation by solving integral equations for the RDF and comparing the results with relevant data. There is a possibility, however, of posing the inverse problem, namely, to reconstruct the form of the interparticle potential from the known RDF. Mikolaj and Pings [78,79] pointed out that besides yielding the potential, the realization of such a program makes it possible to verify by direct experiment the equations for the RDF. If we solve the PY and HNC equations relative to the potential  $\Phi$ , we obtain

$$\Phi_{\text{PY}}(r) = kT \ln \{ [g(r; T, n) - C(r; T, n)] / g(r; T, n) \},$$

$$\Phi_{\text{HNC}}(r) = kT \ln \{ g(r; T, n) - 1 - C(r; T, n) - \ln g(r; T, n) \}.$$

If the PY and HNC equations are correct, then the obtained potentials should not depend on the density and temperature when the values of  $g(r)$  and  $C(r)$  are sub-

stituted in the right-hand side. They turn out, however, to depend on the thermodynamic state of the system [78,79]. Mikolaj and Pings investigated the scattering of x-rays by argon near the critical point. Using these experiments, they reconstructed with the interparticle potential the aid of the PY equation and noted that  $\Phi_{\text{PY}}(r)$  depends on the density (Fig. 7a). The figure shows plots of the potential energy, obtained from the PY equation at different densities for the  $-110^\circ\text{C}$  isotherm of liquid argon. The depth of the potential well was found to be  $-120^\circ\text{C}$  at a density  $0.280 \text{ g/cm}^3$  and  $-90^\circ\text{C}$  at  $0.780 \text{ g/cm}^3$  (the critical density of argon is  $0.536 \text{ g/cm}^3$ ).

The quantitative aspect of these data should be treated with a certain caution, since it is well known that the accuracy of experiment on x-ray scattering is low and can lead to appreciable errors in the determination of the structure factor (and consequently also  $\Phi(r)$ ) [80]. The correctness of the qualitative picture of the potential, however, is not subject to any doubt. It can be assumed that the change of the depth of the potential well is due to the inaccuracy of the PY equation at the investigated densities. The validity of this assumption can be easily verified, since we have at our disposal exact data on the RDF and on the structure factor, calculated by the MD method for a Lennard-Jones liquid. If we regard this structure factor as experimental and reconstruct  $\Phi(r)$  on its basis using the PY equation, then the potential obtained in this manner differs only insignificantly from the initial LJ potential in the temperature interval of interest. Thus, for  $T^* = 1.33$  and  $n^* = 0.4$ , the depth of the well of the calculated potential is only 1% lower than the depth of the well of the LJ potential in the region of the minimum. To be sure, at large distances the calculated potential is deeper than the initial one. However, in any case the error does not exceed 4%. Therefore the decrease of the depth of the potential well with increasing density cannot be attributed in this density interval to the inaccuracy of the PY equation. To interpret such experiments it is apparently necessary to assume that the observed dependence of potential on the density is due to the increasing role of multiparticle interactions with increasing density of the liquid. From this point of view, the LJ potential should be regarded as a certain effective potential that takes correct account of all the interactions at not too high densities, and becomes unsatisfactory at high densities.

In concluding this section, we present plots of a potential obtained from the RDF (determined by the MD method) using the PY equation at different temperatures and densities (Fig. 7b). The LJ potential that should be obtained if the PY equation were exact is shown by the dashed curve. We see that at densities above critical

Table VII

$n^*$	$T^* = 1.3$		$T^* = 1.4$		$T^* = 1.5$		$T^* = 2.0$	
	Experiment	Theory	Experiment	Theory	Experiment	Theory	Experiment	Theory
0.10	0.070	0.071	0.075	0.075	0.078	0.079	0.089	0.09
0.20	0.097	0.098	0.113	0.114	0.125	0.127	0.167	0.169
0.30	0.106	0.105	0.136	0.137	0.161	0.164	0.250	0.254
0.40	0.115	0.118	0.164	0.170	0.207	0.215	0.362	0.369
0.50	0.153	0.172	0.233	0.249	0.303	0.317	0.546	0.552
0.60	0.311	0.326	0.431	0.437	0.535	0.532	0.881	0.865

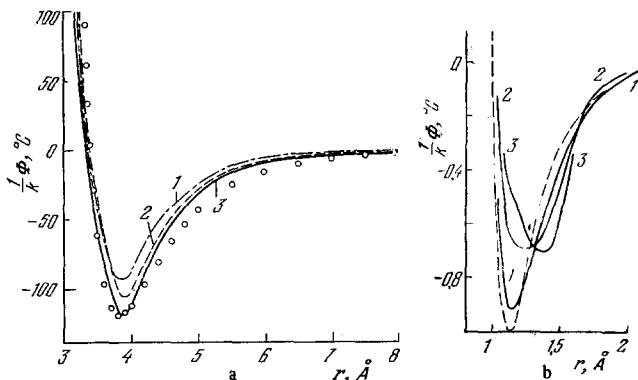


FIG. 7. Potential energy curves for Ar, obtained from the PY equation: a) for different densities at  $T = 110^\circ\text{C}$  (circles—experimental points for an LJ potential with parameters  $\sigma = 3.405\text{\AA}$ ,  $\epsilon/k = 119.8^\circ\text{K}$ ;  $\rho = 0.780$  (1),  $0.536$  (2) and  $0.280\text{ g/cm}^3$  (3) [79]), b) with RDF calculated by the MD method [11] (1— $T^* = 1.328$ ,  $n^* = 0.5426$ , 2— $T^* = 1.05$ ,  $n^* = 0.75$  and 3— $T^* = 1.127$ ,  $n^* = 0.85$ ).

the PY equation does not result in a correct determination of the two-particle interaction.

c) **The problem of self-consistency of the liquid pressure.** From the foregoing review of the numerical solutions of the PY equation and equations related to it it is seen that the quality of the obtained results can be regarded as good or satisfactory for estimates of the RDF, the energy, and the entropy, but unsatisfactory for estimates of the pressure and compressibility in the liquid state proper. The main reason is the inconsistency of the two expressions for the pressure (or compressibility) defined by Eqs. (1) and (3) when the approximate function  $g(r)$  is used. This defect is inherent in all the known approximate liquid-state theories based on the study of the RDF. There is a known analytic condition for the self-consistency of the pressure [81,82]:

$$n \int r \Phi'(r) g(r) dr + (n^2/2) \int \int [F_3(r, \rho) - g(\rho)] \rho \Phi'(r) dr d\rho = 3kTn \int \int [g(r) - 1] dr.$$

It contains explicitly the three-particle distribution function and cannot be used directly in the PY or HNC scheme. It can be used in principle, however, to construct correct theories in the higher approximations, analogous to PY-2 and PY-II.

Considerable progress in the calculation of the equation of state of a simple liquid was attained recently in another way. We have already noted that the internal energy calculated by the PY equation with LJ potential differs from the exact value by approximately 2.5% at low temperatures, and that this error decreases with increasing temperature (see Table VI). Such good agreement between the results of calculation and the exact values suggests the use of the energy equation (2) to obtain the equation of state. To this end it suffices to use the well-known thermodynamic relation between the energy and the free energy  $F$ :

$$E = -T^2 \partial(F/T) / \partial T.$$

If we integrate this equation with respect to the temperature, we can express the free energy in terms of the RDF with the aid of (2). Differentiating furthermore  $F$  with respect to  $n$ , we obtain the pressure as a func-

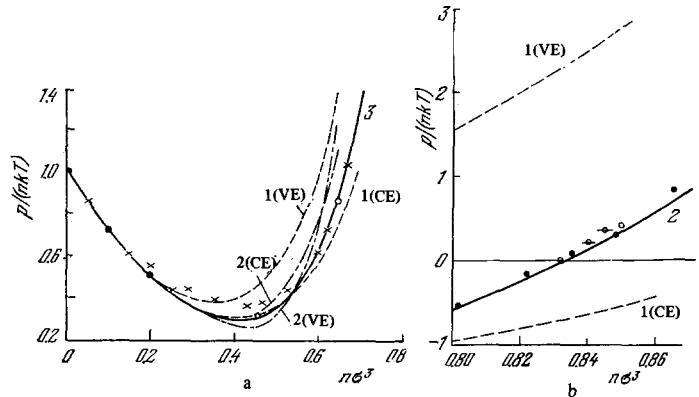


FIG. 8. Equation of state of Lennard-Jones liquid according to PY: a)  $T^* = 1.38$  isotherm (light and dark circles—results of exact computer calculations, crosses—experimental results [85]; 1—PY, 2—PY-2, 3—PY(2)); b)  $T^* = 0.72$  isotherm (dark and light circles—results of exact computer calculations, circles with dashes—experimental points [85]; 1—PY, 2—PY(2)).

tional of  $g(r)$ , i.e., the required equation of state. Practical realization of this program has indeed demonstrated the advantage of the energy equation (2) over Eqs. (1) and (3). Thus, the values of the fourth and fifth VC calculated in this manner in [83] using an LJ potential are much better than those obtained by using the VE or CE; they are almost as accurate as in the PY-II theory (but the latter require much more laborious numerical calculations). This question was investigated in greater detail by Barker, Henderson, and Watts [84,85]. They calculated the thermodynamic properties of a system with LD potential on the basis of the energy equation (2) and found that, in a wide range of temperatures and densities, the PY equation predicts very well the thermodynamic characteristics of the system, namely the energy, the specific heat, the equation of state, the entropy, and the liquid-vapor coexistence curves. By way of illustration, we present the equation of state of a Lennard-Jones liquid at two temperatures (Fig. 8). It can be easily concluded that calculation by Eq. (2) greatly improves the agreement between the theoretical and experimental results.

The reason why the PY equation in conjunction with the energy equation (2) leads to such good results (in comparison with the VE or CE) becomes more understandable if one turns to the already mentioned Barker-Henderson perturbation theory. In this theory, the interparticle potential of an arbitrary system is broken up into a sum of two terms, one of which is in a certain sense smaller than the other and is regarded as a perturbation. The free energy of the system (and with it also all the thermodynamic functions) is expanded in powers of the "perturbing" potential, and the unperturbed terms chosen to be the hard-sphere potential. If such an expansion is carried out for the RDF, then it turns out [83] that the  $n$ -th order term in  $g(r)$  leads to  $n$ -th order terms in the thermodynamic properties, if one uses the VE or the CE. However, when the energy equation is used, the  $n$ -th order term in  $g(r)$  causes the thermodynamic quantities to be calculated more accurately, accurate to terms of order  $(n + 1)$  inclusive. Thus, using as the zeroth approximation in the RDF its approximate value obtained from an analytic solution of

the PY equation for hard spheres, we obtain with the aid of the VE or the CE the thermodynamic characteristics likewise in the zeroth approximation, whereas the use of the energy equation leads to the contributions to the thermodynamic quantities accurate to first order. The resultant difference for the thermodynamic quantities may turn out to be appreciable, since the zeroth and first-order terms in this theory are of the same order of magnitude, whereas the higher-order corrections are small<sup>[38,39]</sup>.

c) **Phase transitions in the Percus-Yevick theory.** An important role in the estimate of the suitability of the PY theory is played by the question of the accuracy with which this theory describes phase transitions in which a liquid phase participates. The theory is called upon to describe the stability limit of the liquid relative to crystallization, to predict the existence of the critical point with acceptable estimates of the critical parameters, and an approximate description of the liquid-gas transition at temperatures below critical.

In the method of integral equations one deals only with a homogeneous phase, gas or liquid, as implied already in the initial equations when the conditions  $F_1(\mathbf{r}) = 1$  and  $F_2(\mathbf{r}, \mathbf{r}') = g(|\mathbf{r} - \mathbf{r}'|)$  are assumed. Therefore the liquid-crystal transition cannot be discussed here without introducing additional information on the crystalline phase. It is possible, however, to formulate the problem of the stability limit of the liquid with respect to crystallization. This question was investigated in the superposition approximation and described in detail in<sup>[2]</sup>. The problem was not investigated for the PY and HNC equations and for realistic interaction potentials. We shall stop to discuss only the hard-sphere model in accordance with the PY equation. From numerical calculations by the MC and MD methods it is known that compression produces in an equilibrium system of hard spheres a first-order phase transition of the dense gas-crystal type near  $\eta_{\text{cr}} = 0.64$ <sup>[57]</sup>. For a theoretical estimate of  $\eta_{\text{cr}}$  it is necessary to turn to the asymptotic form of the function  $h(r)$  as  $r \rightarrow \infty$ <sup>[2]</sup>. Putting in (35)  $h(r) = \varphi(r)/r$ , we obtain a homogeneous equation for  $\varphi(r)$

$$\varphi(x) + 12\eta \int_0^1 \tau_0(s) ds \int_{|x-s|}^{x+s} \varphi(t) dt = 0, \quad x \gg 1,$$

with solutions in the form

$$\varphi(x) \sim e^{-\alpha x} \cos(\beta x + \gamma).$$

The stability limit of the homogeneous phase corresponds to a value  $\eta = \eta_{\text{cr}}$  such that the smallest  $\alpha = \alpha(\eta)$  vanishes<sup>[2]</sup>. A computer numerical analysis of the problem leads to a value  $(\alpha/D)_{\text{min}} \sim 10^{-3}$  for  $\eta \approx 0.64$ , but zero is never reached at any value of  $\eta$ . This is apparently sufficient for a phase transition (i.e., for the ordered phase to be more stable than the homogeneous phase), but insufficient for the appearance of an exact stability limit. The smallness of  $(\alpha/D)_{\text{min}}$  suggests that even a slight refinement of the PY equation, for example in the spirit of PY-2 or PY-II, would lead to a value  $(\alpha/D)_{\text{min}} = 0$  in the same vicinity of  $\eta_{\text{cr}} \approx 0.64$ , in accord with the "experimental" value from<sup>[57]</sup>. We note that the solution of a similar problem in the superposition approximation leads to a value

Table VIII

$R$	$3.5\sigma$	$5.0\sigma$	$6.0\sigma$
$T_{\text{cr}}^*$	1.275	1.305	1.315
$\eta_{\text{cr}}^*$	0.268	0.276	0.278

$\eta_{\text{cr}} = 0.5$ , which differs considerably from the value in<sup>[57]</sup>.

The existence of solutions of the PY equation for hard spheres at  $\eta > \eta_{\text{cr}}$  is discussed in<sup>[86,87]</sup>. Such formal solutions actually do exist, but no definite physical meaning can be ascribed to them.

The liquid-vapor phase transition calls for the existence of attraction between the particles. The simplest model of this kind is the model of hard spheres with surface adhesion of the particles, which admits of an analytic solution of the PY equation. An analysis of this problem does indeed lead to the existence of a critical point and a liquid-gas first-order phase transition below the critical temperature<sup>[37]</sup>. The pressure isotherms above and below the critical point and the phase-transition line turn out to be qualitatively the same as for real systems, if the VE is used as the equation of state.

For more realistic potentials, numerical integration of the PY equation leads to analogous results<sup>[77,88,89]</sup>. Using an LJ potential cut off at a certain distance  $R$ , it was observed that when the behavior of the direct correlation function  $C(r)|_{T=0}$  is investigated as a function of the density  $n$ , then the PY equation has one physically meaningful solution above a certain temperature  $T_{\text{cr}}$ . At the temperatures  $T < T_{\text{cr}}$  there exists a density region for which the PY has no solutions, but outside this region a solution exists again. If we draw the isotherms in the different temperature regions (Fig. 9), they turn out to be qualitatively similar to the isotherms of real matter, and the isothermal compressibility becomes infinite on the isotherm corresponding to  $T_{\text{cr}}$ . This fact can be naturally interpreted in the sense that the thermodynamic states for which the PY equation has

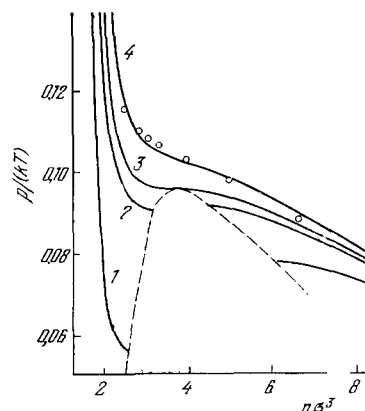


FIG. 9. Equation of state of a Lennard-Jones liquid on the basis of the PY equation in conjunction with the VE. Circles—experimental values for Ar at  $T^* = 1.3$ ; the dashed curve outlines the region where the PY equation has no solutions:  $R = 3.5\sigma$ ,  $T^* = 1.2$  (1), 1.263 (2), 1.275 (3), and 1.3 (4)<sup>[86]</sup>.

no solutions correspond to the two-phase region, and  $T_{cr}$  has the meaning of the critical temperature. If the isotherms are calculated with the aid of the VE, then the compressibility does not become infinite on the critical isotherm.

Figure 9 shows also the experimental points along the isotherm  $T^* = 1.34 Ar$ . Even in the region of the critical density, the experimental and calculated values agree within 2%. It should be noted, however, that the thermodynamic properties calculated from the PY equation turn out to depend on the value of  $R$  at which the LJ potential is cut off. At  $R = 3.5 \sigma$ , the equation of state obtained from the VE agrees very well with the data on Ar. If  $R$  is increased to  $5\sigma$  or  $6\sigma$ , then the agreement becomes poor, and the critical temperature rises. The critical density is not strongly altered in this case (see Table VI, which shows the values of the critical constants for systems with LJ potentials cut off at a distance  $R^{[88]}$ ).

The numerical solution of the HNC equation with the same cut-off LJ potential also reveals the presence of a phase transition. The behavior of the thermodynamic functions predicted by the HNC, however, differs strongly from the corresponding experimental data<sup>[89]</sup>. In particular, the compressibility of the liquid does not become infinite at the critical point.

There is therefore no doubt that the PY equation and the equations related to it are suitable for the approximate description of phase transitions in which a liquid phase participates and of critical phenomena. Nonetheless, by virtue of the approximate character of the theory, we cannot count here on exact descriptions of real systems. This is most clearly seen with the calculation of the specific heat  $c_v$  with the aid of PY (from the energy equation) as an example<sup>[85]</sup>. A significant feature of the calculations is the observation of a maximum of the specific heat in the critical region. The plots of the specific heat against the density at fixed temperature, being monotonic far from the critical state, become nonmonotonic when  $T^* = 1.3$  is approached and have clearly pronounced maxima. It is stated in<sup>[85]</sup> that it can be shown analytically that the specific heat as a function of the temperature has at a density equal to the critical value a singularity of the type

$$c_v \sim (T - T_{cr})^{-1/2}.$$

We note that in the model of spheres with surface adhesion the specific heat has a similar singularity. Therefore such a dependence of  $c_v$  on  $T$  near the critical point is apparently inherent in the PY theory and does not depend on the form of the interparticle-interaction potential. The obtained dependence is qualitatively quite satisfactory and the observed singularities can be regarded as a success of the PY theory. However, such a strong singularity does not agree with the modern experimental and theoretical data on the behavior of real matter in the immediate vicinity of the critical point. The PY theory cannot describe fine details of the behavior of thermodynamic functions near the critical point. For a more accurate description of the critical phenomena in the method of integral equations it is necessary to change over to still unknown equations of a more complicated type.

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Translated by J. G. Adashko