ADVANCES IN CHEMICAL PHYSICS

VOLUME 139

Series Editor

STUART A. RICE

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and
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ADVANCES IN CHEMICAL PHYSICS

VOLUME 139

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CONTRIBUTORS TO VOLUME 139

PAUL BLAISE, Laboratoire de Mathématiques, Physique et Systèmes, Université de Perpignan, 66860 Perpignan Cedex, France

JEAN-MARC BOMONT, Laboratoire de Physique des Milieux Denses, Université Paul Verlaine, 57078 Metz, France

OLIVIER HENRI-ROUSSEAU, Laboratoire de Mathématiques, Physique et Systèmes, Université de Perpignan, 66860 Perpignan Cedex, France

MARK N. KOBRAK, Department of Chemistry, Brooklyn and the Graduate Center of the City University of New York, Brooklyn, NY 11210 USA

FRANÇOIS O. LAFORGE, Department of Chemistry and Biochemistry, Queens College—CUNY, Flushing, NY 11367 USA

MICHAEL V. MIRKIN, Department of Chemistry and Biochemistry, Queens College—CUNY, Flushing, NY 11367 USA

UDAYAN MOHANTY, Eugene F. Merkert Chemistry Center, Department of Chemistry, Boston College, Chestnut Hill, MA 02467-3800 USA

ALEX SPASIC, Baker Laboratory of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301 USA

PENG SUN, Department of Chemistry and Biochemistry, Queens College—CUNY, Flushing, NY 11367 USA

ALBERT STOLOW, Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa ON K1A 0R6, Canada

JONATHAN G. UNDERWOOD, Department of Physics and Astronomy, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK

INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

STUART A. RICE

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RECENT ADVANCES IN THE FIELD OF INTEGRAL EQUATION THEORIES: BRIDGE FUNCTIONS AND APPLICATIONS TO CLASSICAL FLUIDS

JEAN-MARC BOMONT

Laboratoire de Physique des Milieux Denses, Université Paul Verlaine,
57078 Metz, Cedex 3, France

CONTENTS

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ABSTRACT

We offer a nonexhaustive presentation of the advances in the field of the integral equation theories (IETs) in terms of bridge functions, by describing their application to the determination of structural and thermodynamic properties of simple fluids. After having exposed some basic necessary definitions in the structural description of fluid systems, various IETs are first presented, by recalling their basic expressions and underlying physical assumptions. In this context, a special attention is devoted to the thermodynamic consistency concept, and to the role that this natural constraint plays with the improvement of their performances. In this framework, we shall have as a specific purpose in this presentation to investigate the *r*– and *q*–space structural predictions of the IETs together with their relationship with thermodynamics. It is already known that these older theories, that provide in principle a direct source of information, yield however only qualitative agreement for correlation functions, because of suffering of a severe thermodynamic inconsistency. Improved closure relations, the self-consistent integral equation theories (SCIETs) are then introduced. Their applications are examined and systematically compared against related computer simulation data, when available. Satisfying to a single thermodynamic consistency condition provides better correlation functions, but this criterion is not always necessarily sufficient in obtaining accurate description of bridge functions, that are shown to be sensitive to the long-range part of the potential. Introducing supplementary tools, like partitioning schemes for the interaction potential, is needed. Furthermore, the calculation of the excess chemical potential and of the related entropic quantities requires the best possible bridge function $B(r)$ and, at least, the fulfilment of a second thermodynamic consistency condition. In this framework, recent developments are presented. Among numerically solvable theories, only few of them turn out to be accurate in the reproduction of the correlation functions up to the bridge function. These SCIETs are capable of providing accurate predictions for fluid models as compared to simulation calculations. The accuracy of theoretical predictions is also discussed for real systems involved with many-body forces with the aim of systematic assessment of theories. The q–space structural predictions of the latters are of primary importance since they are measurable quantities. In order to provide a complete scenario of calculations in classical fluids, both thermodynamic and structural properties are usually presented in parallel with the available experimental measurements and with computer simulation data.

I. INTRODUCTION

The primary goal of liquid theory is to predict the macroscopic properties of classical fluids from the knowledge of the interaction potential between the constituent particles of a liquid. This area is a very challenging task, because liquids are of vital interest for technology, physics, and chemistry, and for life itself. Seventy years ago, the very existence of liquids seemed a little mysterious. Today, one can make fairly precise predictions of the microscopic and macroscopic static properties of liquids. More than a century of effort since the pioneering work of van der Waals has led to a complete basic understanding of the physicochemical properties of liquids. Advances in statistical mechanics (integral equations, perturbation theories, computer simulation), in knowledge of intermolecular forces and in experimental techniques have all contributed to this. In this presentation, we will be concerned with recent advances in the liquid theory devoted to the description of simple classical fluids properties as determined by means of integral equation theories (IETs).

The availability of a satisfactory theory for simple fluids properties means that these last can successfully be predicted and described at the microscopic statistical mechanics level. This means, once the interparticle law force for a certain fluid has been fixed, one in principle should be able to determine, by means of exact equations relating the interaction potential to some structural functions and thermodynamical quantities, the properties the system will exhibit. However, in practice, a certain number of approximations need to be done in such a theoretical approach, which can be recalled according to the following uncontournable aspects:

1. In order to study a system, one first has to assume a model interaction potential between the particles that are defined as the constituents of the fluid under investigation. Such a modelization is necessary if it is desired not to perform a quantum mechanical description of the system at the level of a first principle Hamiltonian composed of elementary forces. In the latter case, the *ab initio* molecular dynamics technique, developed by Car and Parrinello [1, 2], was revealed to be a powerful investigation tool that was adopted by many authors the last two decades.
2. The physical properties of the fluid model are then calculated through either classical computer simulation techniques, or by some adequate liquid-state theories.

On the one hand, as far as classical computer simulation is concerned, this kind of approach provides, for a given potential model, virtually exact results for structural and thermodynamic properties accompanied with a statistical error, which essentially is due to the use of a finite number of particles [3 and references cited therein]. However, the evaluation of desired quantities requires considerable computational times. Other difficulties arise in the simulation of near critical thermodynamic states, since correlations between the constituents tend to extend over "infinite" distances while the simulation cell edge is at most a few ten angströms [4]. However, despite these problems, it is observed that considerable progresses have been made recently in the simulation calculations thanks to a number of computational strategies derived by several authors together with the increasing power of computers. Nowadays, large-scale simulations [5], in which the calculation of the forces are parallel, allow us to simulate systems with an increasing number of particles in the cell and are suitable to study physical systems involved with many-body forces.

On the other hand, equilibrium statistical mechanics offers appropriate theoretical tools for a complete microscopic determination of properties under interest. In fact, basic thermodynamic quantities, such as pressure and internal energy, wherefrom most of the other thermodynamic quantities involved in the description of the fluid can be determined, are expressed in terms of a structural function that measures the degree of correlation between pairs of particles [6]. For a homogenous and isotropic system, this is the well-known "pair correlation function" (pcf) $g(r)$. Integral equation theories for the liquid structure, whose purpose is to determine this function, have developed rapidly in the late 1980s and early 1990s from atomic to more complex systems. The pcf, which describes the local arrangement of particles, is in fact related to the interparticle potential by exact equations that involve the so-called "bridge function" $B(r)$ [7], which, as will be seen further, is expressed as a density ρ infinite series weighted in terms of irreductible diagrams. Unfortunately, it is not expressed in terms of the pcf itself in a closed form. At this stage, some approximations must be introduced in order to solve the structural problem. To study this problem, an integral equation is typically generated in which the pcf $g(r)$ (or some other structural function closely related to it) is the *a priori* unknown function to be determined. It is obvious from what has been said that the IETs introduce in the description of a fluid model a certain degree of approximation with respect to the "exact" computer simulation treatment. Therefore, thermodynamic and structural properties predicted by the theories must be conveniently and systematically assessed against the corresponding results provided by molecular dynamics (MD) or Monte Carlo (MC) calculations. For a long time, these IETs have suffered from a fundamental shortcoming, the lack of an accurate closure relation [8]. Hence, the integral equation method has seemed to be a relative weak field among its sister methods.

Nevertheless, as will be seen, IETs possess their own peculiarities that make them an irreplaceable tool of investigation of the fluid state. In fact, note first that the approximations made within IET about the form of the pair correlation function, and about its relationship with the potential either amount to, or explicitly express, some simplifying representation of the full many-body structural problem [7, 9–11]. In this respect, comparison with the simulation results possibly followed by that with experimental data for some real system mimicked by the model also implies a test of the hypothesis made on structural correlations and of the physical picture adopted. Also, the solution of an IET is not in general conditioned to the use of a finite system, as it happens with simulation. This advantage is very precious. It allows us, for example, to obtain in a very short time results at the low wavelength limit that can be directly compared to Small Angle Neutron Scattering (SANS) measurements [12–15], while the numerical simulation requires the treatment of very large cells, with increasing large execution times. Quite frequently, IETs can be solved only through numerical procedures that require the use of spatial grids whose extent is by necessity finite. The grid size, however, is generally much larger than typical simulation box sizes. Moreover, such numerical solutions usually do require shorter computational times than comparably accurate simulations. Another advantage of IETs is that these theories can be inverted. Contrary to the usual scheme, where the structure is calculated from a hypothetical interaction potential, the inverted method [16] allows us to determine with a reasonable accuracy an effective potential from the experimental structure factor $S(q)$, that is the Fourier transform of $g(r)$. It is not difficult to guess that the more the IET is accurate, the more the extracted inverted potential is confident. This scheme has proved to be a precious source of information for atomic fluids, and is somehow the counterpart of the Car–Parrinello approach.

It is probably an understatement to say that the quest in integral equation studies is the search for accurate closures. Perhaps closures constitute the most obstreperous bottleneck in achieving high accuracy and furthering advances for IETs. The study of $B(r)$ and the development of new and better closure relations for this function have been the subject of increasing interest. As attested in the literature, this is over the two last decades that several attempts have been made to improve upon these closure relations and to extend the range of validity of integral equation theory. As seen in the following sections, the ''bridge function'' is one of the keywords in liquid theory. For example, the configurational chemical potential depends explicitly on the bridge function $B(r)$ and has been shown [8] that its calculation is mainly affected by the contribution of $B(r)$ inside the core region (98% in the case of hard-sphere fluid). That is one of the reasons why a detailled knowledge of the bridge function is crucial to perform such a calculation.

Answers to the following questions are sought. (1) Can a closure, or several closures, be found to satisfy theorems for simple liquids? (2) If such closures exist, will they be improvements over conventional ones? Do they give better thermodynamic and structural information? (3) Will such closure relations render the IE method more competitive with respect of computer simulations and with other methods of investigation?

Here, we propose to give an overview of the present status of the applications of self-consistent integral equation theories (SCIETs) aimed to predict the properties of simple fluids and of some real systems that require pair and many-body interactions. We will not therefore be concerned with a number of attempts that have been achieved by various authors to extend the IETs approach to fluids with quantum effects, either with several existing studies of specific systems, as, for example, liquid metals, whose treatment yields a modification of the IETs formalism. Our attention will be restricted to simple fluid models, whose description is, however, an essential step to be reached before investigating more complex systems.

In order to introduce basic equations and quantities, a preliminary survey is made in Section II of the statistical mechanics foundations of the structural theories of fluids. In particular, the definitions of the structural functions and their relationships with thermodynamic quantities, as the internal energy, the pressure, and the isothermal compressibility, are briefly recalled together with the exact equations that relate them to the interparticular potential. We take advantage of the survey of these quantities to introduce what is a natural constraint, namely, the thermodynamic consistency.

In Section III, a number of nonconsistent IETs is first introduced together with their numerical solution procedures or, when available, with their analytical solutions. The accuracy of each envisaged theory is also shortly summarized. Then, the problem of the thermodynamic consistency preliminarily addressed in Section II is fully developped together with the SCIETs. Reference is made to very recent works.

Specific results of the SCIETs for fluid models, including thermodynamic concepts and quantities necessary to describe phase equilibria, are reported in Section IV. In particular, a section is devoted to recent developments in the calculations of the excess chemical potential and related entropic quantities.

The extension of SCIETs to the many-body interactions is presented in Section V. Rare gases, whose constituents interact through three-body forces, are a test case to examine the validity of the SCIETs in describing real systems. Again, the problem of the thermodynamic consistency is covered in this section, since recent SANS measurements provide the structure factor *S(q)* at very low–q and allow us to deduce the strength of the three-body interactions. A direct comparison of the theoretical results against sharp experiments is feasible. The conclusions are given in Section VI.

II. CLASSICAL STATISTICAL MECHANICS FOR LIQUID STATE

A. Pair Correlation Function and Thermodynamics Quantities

The liquid state of a material has a definite volume, but it does not have a definite shape and takes the shape of a container, unlike that of the solid state. Unlike the gas state, a liquid does not occupy the entire volume of the container if its volume is larger than the volume of the liquid. At the molecular level, the arrangement of the particles is random, unlike that of the solid state in which the molecules are regular and periodic. The molecules in the liquid state have translational motions like those in a gas state. There is short-range interparticular ordering or structure, however.

Briefly, we recall some basic definitions involving the short-order structural functions typical of the liquid state and their relationships with thermodynamic quantities. Considering a homogenous fluid of N particles, enclosed in a definite volume V at a given temperature T (canonical ensemble), the two-particles distribution function [7, 9, 17, 18] is defined as

$$g^{(N)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{Z^{(N)}} V^2 \int \ldots \int \exp[-\beta u(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)] d\mathbf{r}_3 \ldots d\mathbf{r}_N \qquad (1)$$

where $\mathbf{r}_1,\ \mathbf{r}_2,\ldots,\mathbf{r}_N$ denote the set of $3N$ spatial coordinates of the N particles and $u(\mathbf{r}_1,\ \mathbf{r}_2,\ldots,\mathbf{r}_N)$ is the total potential energy. The partition function expressed as

$$Z^{(N)} = \int \ldots \int \exp[-\beta u(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)] d\mathbf{r}_1 \ldots d\mathbf{r}_N \qquad (2)$$

and $\beta = (k_B T)^{-1}$ is the inverse temperature. According to Eq. (1), $g^{(N)}(\mathbf{r}_1,\ \mathbf{r}_2)$ measures the probability of finding the particle labeled 1 in a volume $d\mathbf{r}$ at $\mathbf{r}_1$, and the particle labeled 2 in a volume $d\mathbf{r}$ at $\mathbf{r}_2$, irrespective of the positions of the $N-2$ remaining particles. The appearance of the factor V^2 in Eq. (1) results of a normalization to $1/V^2$, which is the probability of obtaining the same configuration of particles in the absence of correlations. In this case, each particle has the probability $1/V$ of occupying any position in the volume V. In this framework, it turns out that when the distance between particles 1 and 2 tends to infinity, $g^{(N)}(\mathbf{r}_1,\ \mathbf{r}_2)$ tends to 1. This expresses the loss of correlation between particles at large distances. If the system is not only homogenous, but also isotropic, $g^{(N)}(\mathbf{r}_1,\ \mathbf{r}_2)$ depends only on the distance $|\mathbf{r}_1 - \mathbf{r}_2| = r$, that is to say that $g(\mathbf{r}_1,\ \mathbf{r}_2) = g(r)$. In this case, the latter structural function is known as the pair correlation function, which measures the probability that given a particle at the origin, another particle of the fluid can be found at a distance r from it (see Fig. 1). In the following, we will focus our attention on the determination of $g(r)$ as a solution of integral equations. We will restrict our attention first to systems of particles that interact through central pair forces (an extension to many-body interactions is presented in Section V) for which the total potential energy can be written as a sum of pairwise additive terms, so that

$$u(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{2}\sum_{i \neq j} u_2(\mathbf{r}_{ij}) \tag{3}$$

where $r_{ij} = |r_i - r_j|$ and $i,\ j = 1, \ldots, N$. In this case, it is easy to prove that the excess internal energy per particle is given by

$$\frac{E^{\mathrm{ex}}}{N} = 2\pi\rho \int g(r)u(r)r^2 dr \tag{4}$$

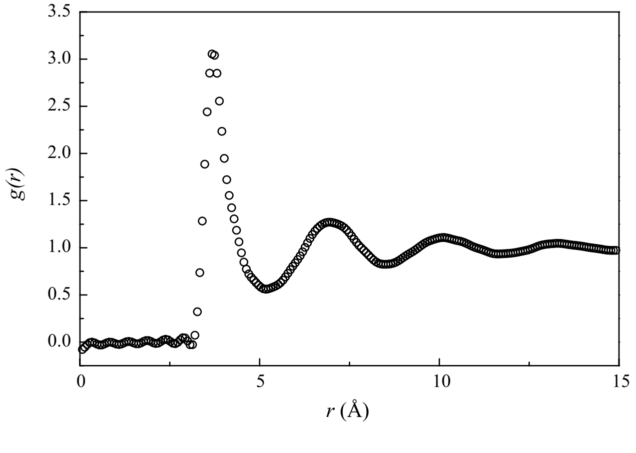

Figure 1. Neutron-scattering experiment result for the pair correlation function $g(r)$ of liquid argon at $T = 85\,\mathrm{K}$ and $V = 28.26\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$, near the triple point. Notice that the ripples at small r are artifacts of the data treatment. Taken from Ref. [19].

while the virial pressure, given by the equation of state (EOS), can be written as

$$\frac{\beta P}{\rho} = 1 - \frac{2}{3}\beta\pi\rho \int g(r) r^3 \frac{du(r)}{dr} dr \tag{5}$$

where $\rho = N/V$ is the average number density of particles in the system. Equations (4) and (5) illustrate the importance of the knowledge of the pcf in order to achieve an estimate of fundamental thermodynamic quantities [7, 9, 17, 18]. Extending Eqs. (1) and (2) to the grand-canonical ensemble case leads to a first indication, but poor one, of the link between the interactions and the structure. It can be shown easily that, in the case of a dilute gas ($\rho \to 0$), one has $g(r) \to e^{-\beta u(r)}$. In this densities regime, the pressure can be formally written

$$\frac{\beta P}{\rho} = \sum_{n=1}^{+\infty} B_{n+1}(T)\rho^n \tag{6}$$

This series is known as the virial expansion, where B_n are the virial coefficients. In principle, these last can be calculated if the potential is known. In practice, however, the calculation is feasible only for the first few coefficients. In this framework, Eq. (6) is only applicable to low density regimes. Obviouly, a complete theory is expected to confidently calculate the highest possible number of known virial coefficients. Such a calculation is one of the benchmarks of its overall accuracy.

Since it is important to judge the accuracy of the description that will be given to the fluid, a third important quantity, the isothermal compressibility χ_T of the system, can be defined via two independent routes. On the one hand, by making use of the thermodynamic fluctuation theory, one obtains

$$\rho k_B T \chi_T = 1 + 4\pi\rho \int [g(r) - 1] r^2 dr \tag{7}$$

This relationship is known as the compressibility equation. On the other hand, from Eq. (5), at a given temperature T one has

$$\chi_T = \frac{1}{\rho} \frac{\partial \rho}{\partial P}\bigg|_T \tag{8}$$

These last relations clearly establish the link between the short ordered structure and the compressibility of the fluid.

B. Pair Correlation Function and Structure Factor

As mentioned above, when the distance separating a pair of particles tends to infinity, the correlations vanish and $g(r)$ tends to 1. That means that the

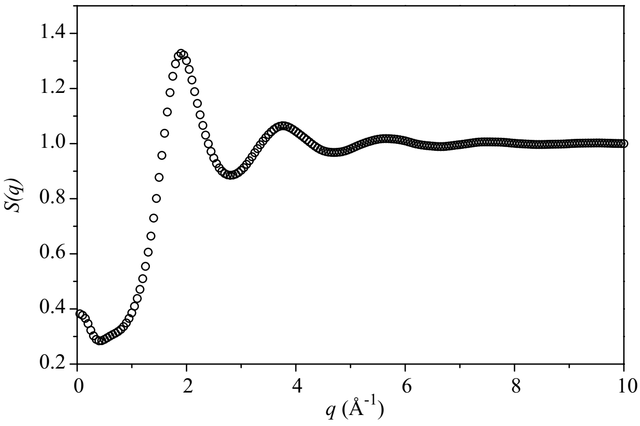

Figure 2. Neutron-scattering experiment result for the structure factor of argon at $T = 350\,\mathrm{K}$ and $\rho = 12.3\,\mathrm{atoms\,nm}^{-3}$. Taken from Ref. [20].

total correlation function defined as $h(r) = g(r) - 1$ tends to 0. For the theory of liquids, the Fourier transforms (FT) of $g(r)$ and $h(r)$ are of useful interest [7, 18]. Actually, they are directly related to the structure factor $S(q)$ that is experimentally measurable by X-ray diffraction or neutron scattering (see Fig. 2). One has

$$S(q) = 1 + \rho \int d\mathbf{r}[g(r) - 1] \exp(-i\mathbf{q}.\mathbf{r}) \tag{9}$$

and

$$S(q) = 1 + \rho h(q) \tag{10}$$

where $h(q)$ is the FT of the total correlation function $h(r)$, so that

$$h(q) = \int d\mathbf{r} h(r) \exp(-i\mathbf{q}.\mathbf{r}) \tag{11}$$

In other words, applying the inverse FT to the measured $S(q)$ leads to the knowledge of the pcf $g(r)$, that is

$$\rho[g(r) - 1] = \frac{1}{(2\pi)^3} \int d\mathbf{q}(S(q) - 1) \exp(i\mathbf{q}.\mathbf{r}) \tag{12}$$

An interesting feature appears from Eqs. (8) and (9). The structure in the q–space is found to be directly related to the thermodynamics since, in the $q = 0$

limit [9, 18], one obtains the striking result

$$S(q = 0) = \rho k_B T \chi_T \tag{13}$$

This relationship corresponds to what is called a *thermodynamic consistency condition*, whose fulfilment is one of the criterions of accuracy of a self-consistent IET: since $S(q = 0)$ is calculated from the structure (9) and χ_T is obtained from the pressure (8), the left-hand side (l.h.s.) and right-hand side (r.h.s.) of the last relation have to coincide with a precision of 1%. This important aspect is developed below.

C. Thermodynamic Consistency: A Natural Constraint

The thermodynamic consistency of IETs has been the subject of several investigations in the past [21]. Since the thermodynamic quantities are derived from integrals over $g(r)$ and $c(r)$, the desired goal is to obtain exact results at both structural and thermodynamic levels. But the reader has to be aware that a theory rendered self-consistent will not necessarily also become exact at each of these levels simultaneously. In principle, the following is the main adopted stategy: One essentially forces the theory to satisfy some equalities for the pressure calculated from the structure.

There are several routes to the determination of $\beta P/\rho$ from the structure. One is given by Eq. (5). A second possibility is offered by the isothermal compressibility

$$\rho \left.\frac{\partial P}{\partial \rho}\right|_T = \frac{1}{\chi_T} \tag{14}$$

In fact, the quantity $1/\chi_T$ can be integrated with repect to the density and along an isothermal path to yield the pressure. We will therefore use the notation $(\beta P/\rho)_c$ to indicate the compressibility EOS so obtained. A third route is based on the use of the excess internal energy E^{ex}, related to the excess Helmholtz free energy F^{ex} by $E^{\text{ex}} = [\partial(\beta F^{\text{ex}}/\partial\beta]_V$. Then, E^{ex} can be integrated with repect to the inverse temperature β along an isochore path to yield F^{ex}. The excess pressure P^{ex} is then obtained as

$$P^{\text{ex}} = -\left.\frac{\partial F^{\text{ex}}}{\partial V}\right|_E \tag{15}$$

The energy EOS so obtained will henceforth be indicated as $(\beta P/\rho)_E$. If the exact $g(r)$, that is if the true pcf of the system is used in Eqs. (4)–(7), then the virial, the compressibility, and the energy EOS should all take the same value.

So, an accurate predictive theory should satisfiy the following equality:

$$\left(\frac{\beta P}{\rho}\right)_v = \left(\frac{\beta P}{\rho}\right)_c = \left(\frac{\beta P}{\rho}\right)_E \tag{16}$$

The fulfilment of this condition is termed as one of the *thermodynamic consistency conditions*. But, doing so requires the use of external information to the theory that cannot be used in a predictive manner. Of course, obtaining a full thermodynamic consistency without resorting to any external data is the practical purpose of self-consistent IETs.

Integral equation theories of $g(r)$ do in general yield only an approximate estimate of this quantity, and hence they are, to more or less extent, thermodynamically inconsistent. In practice, instead of Eq. (16), one prefers to apply the pressure–compressibility $(P - \chi_T)$ condition expressed by

$$\left.\frac{\beta \partial P}{\partial \rho}\right|_T = \frac{1}{\rho k_{\mathrm{B}} T \chi_T} \tag{17}$$

where P is the pressure obtained from the virial EOS and χ_T is the isothermal compressibility as obtained from the fluctuations route. The advantage of Eq. (17) with respect to Eq.(16) relies on the fact that [22] one can verify the consistency for any thermodynamic state without the necessity of performing an integral of χ_T over successive thermodynamic states, as would be the case for the estimate of $(\beta P/\rho)_c$.

Moreover, since Maxwell's equation relates the internal energy to the pressure $(E - P)$

$$\left.\frac{\partial E^{\mathrm{ex}}}{\partial V}\right|_T = T^2 \frac{\partial}{\partial T}\left(\frac{P}{T}\right)_V \tag{18}$$

two consistency conditions in the form of integrals are obtained [23]:

$$I(\rho, T) = \int \left[c(r) - \frac{r}{6}\frac{d\beta u(r)}{dr}\left(2g(r) + \rho\frac{\partial g(r)}{\partial \rho}\right)\right] r^2 dr = 0 \tag{19}$$

and

$$J(\rho, T) = \int \left[u(r)\left(g(r) + \rho\frac{\partial g(r)}{\partial \rho}\right) + \frac{r}{3}\frac{du(r)}{dr}\left(g(r) - T\frac{\partial g(r)}{\partial T}\right)\right] r^2 dr = 0 \tag{20}$$

These obtained equations set the self-consistent relationship between the correlation functions and their derivatives. Vompe and Martynov [24] defined the total thermodynamic consistency (including the $E - P$ and $P - \chi_T$ terms) by stating that the quantity $S(\rho, T) = \omega_1 I^2(\rho, T) + \omega_2 J^2(\rho, T), \omega_i$'s being weight factors, has to be as small as possible for a given thermodynamic state.

Nevertheless, the reader has to notice that the use of the latter two consistency conditions is not always sufficient in obtaining an accurate description of structural functions (e.g., the bridge function) and, consequently, thermodynamics quantities. The problem of identifying and fulfiling at least a second thermodynamic condition is under the scope in this review article. We will turn back to the crucial point of *thermodynamic consistency* in Sections III and IV when discussing the solution of integral equation theories and their application to simple liquids.

III. INTEGRAL EQUATION THEORIES

A. Fundamental Set of Equations for the Structure

1. *Correlations in a Liquid : The Ornstein–Zernike Equation*

The correlation functions play an essential role in the static description of homogenous classical liquids whose particles are taken to interact through an effective pair potential. The starting point of the liquid-state theory, in terms of correlation functions, is the well-known Ornstein–Zernike equation [25]. The total correlation function $h(r)$ defined in Section II is actually a sum of two contributions that is illustrated by the following relationship

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) h(\mathbf{r}') d\mathbf{r}' \tag{21}$$

The first contribution to $h(r)$ is the direct correlation function $c(r)$ that represents the correlation between a particle of a pair with its closest neighbor separated by a distance r. The second contribution is the indirect correlation function $\gamma(r)$, which represents the correlation between the selected particle of the pair with the rest of the fluid constituents. The total and direct correlation functions are amenable to an analysis in terms of configurational integrals clusters of particles, known as diagrammatic expansions. Providing a brief resume of the diagrammatic approach of the liquid state theory is beyond the scope of this chapter. The reader is invited to refer to appropriate textbooks on this approach [7, 9, 18, 26].

By FT (21), one obtains

$$h(q) = \frac{c(q)}{1 - \rho c(q)} \tag{22}$$

where $c(q)$ has a similar definition as $h(q)$. It is easy to show that

$$\rho c(0) = 1 - \frac{1}{\rho k_{\mathrm{B}} T \chi_T} \tag{23}$$

So, $c(q = 0)$ is a finite quantity even when the isothermal compressibility χ_T tends to diverge in the critical region of any fluid. As will be seen, the former quantity is useful, because of being accessible from direct experiment [12] thanks to recent SANS measurements (see Section V). At variance from $g(r)$, the direct correlation function $c(r)$ in not zero inside the core region $(r < \sigma)$ and its knowledge is crucial in this range of distances, since it is directly related to χ_T so that

$$\frac{1}{\rho k_{\mathrm{B}} T \chi_T} = 1 - \rho \int c(r) d\mathbf{r} \tag{24}$$

In other words, $c(r)$ can be directly obtained from the structure factor $S(q)$ by

$$\rho c(r) = \frac{1}{(2\pi)^3} \int d\mathrm{q} \left(1 - \frac{1}{S(q)} \right) \exp(i\mathbf{q}.\mathbf{r}) \tag{25}$$

That means, as for $g(r)$, the direct correlation function $c(r)$ can be, in principle, derived from experiment. As can be seen, the OZ relation deals with *a priori* two unknown functions $h(r)$ and $c(r)$. The cluster expansion provides an important exact feature for $c(r)$ with respect to the potential interaction at large distances $(r \to +\infty)$, with the result

$$c(r) \simeq -\beta u(r) \tag{26}$$

The direct correlation function decays fairly rapidly with the distance. However, this information, which correlates the structure to the interactions in the fluid, is too poor to provide a complete and accurate theory.

In order to remedy this drawback, the OZ equation can be rewritten by the use of an iterative substitution of $h(\mathbf{r}')$ inside the kernel of (21) [7]. A series of integral terms is obtained, with the result

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) c(\mathbf{r}') d\mathbf{r}' + \rho^2 \int\int c(|\mathbf{r} - \mathbf{r}'|) c(|\mathbf{r}' - \mathbf{r}''|) c(\mathbf{r}'') d\mathbf{r}' d\mathbf{r}'' + \cdots \tag{27}$$

here truncated at the second iteration. The chain structure of (27) shows that the OZ equation amounts of describing the total correlation function $h(r)$ between a pair of particles as a sum of different contributions, the first being the direct correlation function $c(r)$ and the rest being the indirect correlations. This algorithm may have difficulties in converging if the input functions (or some starting solutions) one uses are not close enough to the requested solution. Furhtermore, the final solution has to fulfil of course the thermodynamic consistency condition one uses. As observed, the use of this density expansion is not tractable enough in practice to determine $h(r)$ and $c(r)$.

2. *A Necessary Closure Relation : Introduction of the Bridge Function*

From what precedes, it is obvious that in order to determine the latter two correlation functions for a given pair potential $u(r)$, Eq. (21) must be supplemented by an auxiliary closure relation [7, 17, 18, 27] derived from a cluster diagram analysis that reads

$$h(r) + 1 = \exp[-\beta u(r) + h(r) - c(r) + B(r)] \tag{28}$$

Equations (21) and (28) form the fundamental set of equations of the theory of the liquid state and Eq. (28) may be regarded as a definition for $B(r)$. The term $h(r) - c(r) + B(r)$ is the so-called negative excess potential of mean force $\omega(r)$ ([18] and references cited therein). The bridge function $B(r)$ was shown to be the sum of an infinite number of terms, each consisting of integrals whose kernel are products, of increasing order, of correlation functions. This infinite series is graphically represented by so-called "bridge" diagrams, hence the name attributed to $B(r)$. In other words, the diagrams that comprise the negative excess potential of mean force can be classified [28] according to the number of h bonds connected to particle 1,

$$\omega(r_{12}) = \sum_{n=1}^{+\infty} \omega^{(n)}(r_{12}) \tag{29}$$

The h-bond diagrams of $\omega(r_{12})$ cannot contain any articulation pairs, and so the diagrams connecting the root point 2 with the n h-bonds connected to root point 1 do not have nodal points. This definition is just of the $(n+1)$-particle direct correlation function $c(\mathbf{r}_2,\ \mathbf{r}_3, \ldots, \mathbf{r}_{n+2})$ and one has

$$\omega^{(n)}(r_{12}) = \frac{\rho^n}{n!}\int \cdots \int d\mathbf{r}_3 d\mathbf{r}_4 \ldots d\mathbf{r}_{n+2} h(r_{13})h(r_{14})\ldots h(r_{1,n+2})c(\mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_{n+2}) \tag{30}$$

The reader has to notice that $\omega^{(1)}(r_{12}) = h(r_{12} - c(r_{12})$, which is the indirect correlation function $\gamma(r_{12})$. Unfortunately, even if the types of diagrams are known, the resultant series cannot be transformed to any tractable analytical formula or evaluated numerically with a good accuracy. Recently, from the bridge diagram series, simple phenomenological forms for $B(r)$ haven been proposed for the LJ fluid [29]. They present the advantage of bringing some repulsion between particles at short range, and also attraction at longer distances. However, these forms, even if simple, depend on an adjustable parameter that requires external information. Furthermore, they seem to diverge at zero separation $(r \rightarrow 0)$. Similar approach has been presented for the HS fluid [30]. It is shown that the knowledge of the coefficients of the h-bond expansion of $B(r)$ up to order ρ^4 in Eq. (30) requires the evaluation of many of diagrams. For example, the evaluation of the fourth coefficient of $B(r)$ involves 1731 distinct diagrams, and, of course, investigating higher order coefficients would require the treatment of an exponentially increasing number of diagrams. It is easy to understand that the convergence is very slow (if it converges at all). Despite these drawbacks, it is clear that the knowledge of the exact bridge function would close the problem of the *thermodynamic consistency conditions*. Unfortunately, the bridge function has to be approximated in practice. Though a number of theoretical and simulation procedures have been derived in recent years in order to get an approximate estimate of $B(r)$ for different fluid models, the exact bridge function is not known for any system. As will be discuss next, a class of integral equations arises from the joint use of (28) and OZ. In fact, Eqs. (21) and (28) contain three unknown structural functions. Once some sort of approximation is introduced for $B(r)$, then Eq. (28) can be used as a closure relation to OZ. Then, $h(r)$ and $c(r)$ can be determined by solving the set of two nonlinear integral equations.

In order to be competitive with respect to molecular simulation, the purpose of the IETs is to establish a bridge in between semianalytical relations and the numerical methods. By analyzing a large amount of simulation studies, Rosenfeld and Ashcroft [27] concluded in favor of the existence of a "universality" in the short-range structure of a wide class of fluids models. On this basis, they proposed that the bridge function relative to such systems could be parametrized by the HS fluid bridge function. Then, two important thresholds have been crossed when: (1) Carnahan and Startling [31] derived an exact EOS for HS fluid, and (2) Groot et al. [32] obtained an exact construction of the bridge function for HS fluid, by a suitable fit of numerical simulation results. However, the problem has been found to be more complex, since another studies have shown that, outside the region where repulsive core effects are dominant, the bridge function exhibits a "non universal" behavior.

At this stage, undiscutable data, external of the IETs, were necessarily required to shed some light on these peculiar behaviors, which provides exact reference data for more realistic potentials. First, Nicolas et al. [33] derived an EOS for the Lennard-Jones fluid and Johnson et al. [34] provided MD results for the classical thermodynamic quantities. Notice that Heyes and Okumura [35] recently derived an EOS of the Weeks–Chandler–Andersen fluid.

A second important step has been reached by Llano-Restrepo and Chapman [36]. With the aid of the two former EOS, they performed Monte Carlo simulation calculations for this system over several thermodynamic states, to evaluate the direct and indirect correlation functions, and then to extract the bridge function $B(r)$. These results became useful in testing the accurateness of IETs for the Lennard-Jones potential. Since the thermodynamic properties involve integral over the correlation functions, comparison of just the thermodynamic properties could hide, *a priori*, inaccuracies in the theory.

These prior works offered new motivation to several authors, whose purpose was to obtain adequate theories that would be able to match, at last, with simulation results. Huge efforts were made in this direction. Thus, in order to overcome the problem of thermodynamic consistency (or inconsistency), some attempts consisted in performing judicious interpolations between already existing nonconsistent IETs, while others were devoted to improve these last by introducing parameters to render them consistent [37]. This finding is the subject of what follows.

B. Nonconsistent Integral Equations

We present a brief survey of the most employed auxiliary closure relations that have to be used in conjunction with the OZ equation (21) to determine the total and direct functions $h(r)$ and $c(r)$, or closely related functions. We emphasize that for any proposed approximation for $B(r)$ presented below (but PY and MSA, that are analytically solvable), the numerical procedure imposes the adoption of a finite grid of points in r-space over which the structural functions have to be defined. This obviously implies that also the wave vector in q-space is discretized, and the accurateness of the final solution obviously depends both on the overall extent of such grids and on their spacings (i.e., the total number of points used). The rapidity through which a convergent solution can be obtained crucially depends on the solution strategy. Great progresses have been made in this respect mostly as a result of the application of the Newton–Raphson technique [37, 38] that allows us to improve the accuracy of the successive guessed correlation functions.

1. *Percus–Yevick Approximation*

A very popular closure relation is the Percus–Yevick (PY) approximation [39]. For a generic potential $u(r)$, this approximation assumes that

$$c(r) = [1 - e^{\beta u(r)}] \times g(r) \tag{31}$$

In other words, the bridge function corresponding to PY relation reads

$$B(r) = \ln[1 + \gamma(r)] - \gamma(r) \tag{32}$$

The solution of the system formed by Eqs. (21) and (32) is usually obtained thanks to numerical iterative procedures. However, in the special case of hard-sphere (HS) fluid, the solution is found to be analytical. For this system, the potential reads $u(r) = +\infty$ for $r < \sigma$ and $u(r) = 0$ for $r > \sigma$, where σ is the HS diameter. So, it follows that $g(r) = 0$ for $r < \sigma$ and $c(r) = 0$ for $r > \sigma$. This result satisfies the exact asymptotic limit of $c(r)$ at large distances [see Eq.(26)]. Percus–Yevick is a typical candidate for the thermodynamic inconsistency: indeed, the virial and the compressibility EOS provide the following analytic results in terms of the packing fraction η

$$\left(\frac{\beta P}{\rho}\right)_v = \frac{1+2\eta+3\eta^2}{(1-\eta)^2} \quad \left(\frac{\beta P}{\rho}\right)_c = \frac{1+\eta+\eta^2}{(1-\eta)^3} \tag{33}$$

where $\eta = \frac{\pi}{6}\rho\sigma^3$. It appears that the PY virial and compressibility EOS, respectively, underestimate and overestimate the HS simulation results. These last are quite accurately parametrized in terms of a heuristic EOS developed by Carnahan and Starling (CS) [31], which reads

$$\left(\frac{\beta P}{\rho}\right)_{\text{CS}} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{34}$$

This parametrization is usually considered as exact and is useful to test the quality of the results from IETs calculations for the HS fluid. However, another EOS proposal has been provided [40, 41].

$$\frac{\beta P}{\rho} = \frac{1+\eta+\eta^2-2(\eta^3+\eta^4)/3}{(1-\eta)^3} \tag{35}$$

whose predictions compare well with MC results [41].

2. *Mean-Spherical Approximation*

This another popular closure [43] deals with spherical particles fluids that interact through an infinite repulsive potential at short range $u(r) = +\infty$ for $r < \sigma$ and through a tail at longer distances. Similarly to PY, the mean-spherical approximation (MSA) is formulated in terms of an ansatz for the direct correlation function. In this approach, $c(r)$ is supposed to be

$$c(r) = -\beta u(r) \tag{36}$$

in a range of distances larger that the HS diameter. In the limit $r \longrightarrow +\infty$, the behavior of $c(r)$ is correct. Consequently, one also has $g(r) = 0$ for $r < \sigma$. It appears that the domain of validity of Eq. (31) is extended at shorter range distances. This approach can be generalized in the presence of continuous potentials. Obviously, MSA reduces to PY for the HS system and presents an internal inconsistency as well.