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STUART A. RICE

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STUART A. RICE

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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

CONTENTS

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

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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

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

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

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

and $\beta=(k_\mathrm{B}T)^{-1}$ 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

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

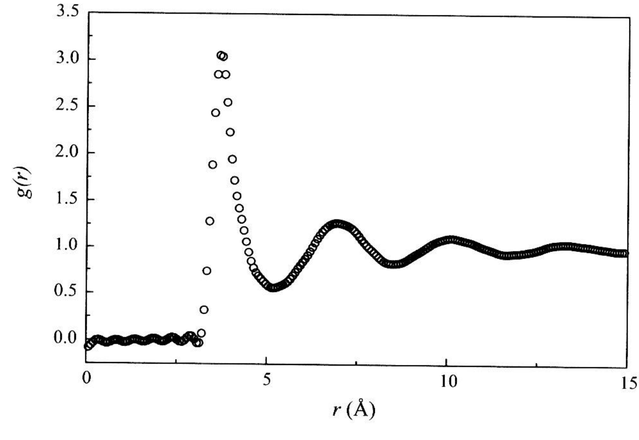

Figure 1. Neutron-scattering experiment result for the pair correlation function $g(r)$ of liquid argon at $T = 85$ K and $V = 28.26\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$, near the triple point. Notice that the ripples at small r are artifacts of the data treatment. Taken from Ref. [19].

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