Revista Mexicana de Física 32 No. 1 (1985) 1-37

DEVELOPMENT OF A THEORETICAL EQUATION OF STATE*

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ABSTRACT

The work developed by the author and his collaborators leading to a theoretical equation of state for real fluids is reviewed. The topics covered in this article are: 1) The van der Waals model and kinetic theory; the model of VDW, molecular collisions and free-volume theory. 2)Perturbation theory and equation of state: perturbation methods in liquids and its relation to the VDW model, exact deduction of the VDW equation and its connection to real fluids. 3) The VDW model and real fluids: intermolecular forces, the inverse problem, the square-well perturbation method, effective parameters and kinetic theory. 4) Corresponding states and systems: generalized corresponding states and systems, their application to real substances and development of the square-well equation of state. And 5) equation of state, fluid mixtures and solutions: solution models, the VDW equation, the square-well perturbation method for mixtures and mixing rules. The main conclusions to be derived from this work are also stated as well as the perspective for future work.

[+] Presentado en la asamblea general ordinaria de la SMF el 29 de marzo de 1984.

RESUMEN

Se revisa el trabajo realizado por el autor y sus colaboradores que ha llevado a una ecuación teórica de estado para fluidos reales. En este artículo se cubren los siguientes tópicos: 1) El modelo de van der Waals y la teoría cinética: el modelo de VDW, las colisiones moleculares y la teoría del volumen libre. 2) La teoría de perturbaciones y la ecuación de estado: métodos perturbativos en líquidos y su relación con el modelo de VDW, deducción exacta de la ecuación de VDW y su relación con fluidos reales. 3) El modelo de VDW y los fluidos reales: fuerzas intermoleculares, el problema inverso, método perturbativo con pozo cuadrado, parámetros efectivos y teoría cinética. 4) Estados y sistemas correspondientes: generalización de estados y sistemas correspondientes para sustancias reales, desarrollo de la ecuación de estado de pozos cuadrados. Y 5) ecuación de estado, mezclas y soluciones: modelos de solución, la ecuación de VDW, método perturbativo de pozo cuadrado para mezclas y reglas de mezclado. Se establecen también las principales conclusiones de estos trabajos y se describe brevemente la perspectiva actual en el tema.

PROLOGUE

This is the story of the research that led to the development of a theoretical equation of state for real fluids. It began in 1969, has involved a score of characters and took place in several laboratories and offices of the Instituto Mexicano del Petróleo (IMP), the Instituto de Investigación en Materiales (IIM) and the Universidad Autónoma Metropolitana (UAM) at Iztapalapa. The background and setting of the story are described in the Introduction, whereas in the later sections the research itself is reviewed. The reader who is not interested in the characters is advised to skip the Introduction and start with the subject matter in section II. As many stories, this one has not come to a real end. The epilogue is still to be written.

I. INTRODUCTION

By the summer of 1969, I had spent a year at the IMP after obtaining my PhD in Berkeley with a thesis on the statistical mechanics of plasmas. My first job was to find out what a physicist is supposed to do in such a place. This question might seem preposterous if the circumstances are not taken into account. One year had been spent to find out that nobody living within 2 000 kilometers knew the answer -although some dared to say they did- and talking to the people that had the problems: the engineers.

A common sense answer to the question was easily confirmed in the literature: In the petroleum and chemical industries there was, and still is, a broad field open to the applications of thermodynamics and statistical mechanics of fluids. By that time, a young physicist had joined in my worries. Together, Luis Ponce and I were able to clear out a few basic things: 1st, the real scientific and practical problems concerned dense fluids, *i.e.*, liquids; 2nd, to tackle these problems a combined theoretical and experimental effort was needed; 3rd, it was indeed not a one man's job, and 4th, it was obviously necessary to establish a foreing connection. These four points led to four inmediate actions: study the physics of liquids and chemical engineering thermodynamics, start a thermodynamics lab, launch a crash program on recruitement and training, and go abroad!

By 1970 the perspective was clearing up. Jakob de Swaan, whom I had met at a thermodynamics conference in Cardiff and was then with the Koninklijke-Shell Laboratorium in Amsterdam, had gallantly scouted our survey of the field of applied thermodynamics, including a brief course that he taught at the IMP. Our "group" had grown in 50% when another physicist, Manuel Guerrero, joined the initial two. I had also obtained a part-time appointment, at the Centro (later Instituto) de Investigación de Materiales of the National University. For several years, the CIM was going to play an important role because it was close to the students we wanted to proselitize.

We had started late but at an exciting time. Fluid-state thermodynamics has two well-defined approaches: on the one side, the statistical mechanics of liquids and gases, and on the other, the thermodynamics equations and data used by the engineers. Both ways were quite developed when we started to look into them, but ours was a peculiar situation. Engineers with experience accumulated in years of design work -plus that of several generations of teachers- can safely, though not wisely, forget about the advances of statistical mechanics and get along with it. A chemical physicist or physical chemist without the direct responsability of pressing practical needs can also forget the more nittygritty realities of empiricism and survive. Our case was different: we didn't have the practical experience but had the responsability. We couldn't forget neither, and also as importantly, we were physicists by training and couldn't forget it either.

Starting a laboratory from scratch proved to be a difficult and slow endeavour. The main experimental lines had been decided on information gathered on a tour of British laboratories and universities (sponsored by the British Council), the Institut Francais du Petrole and the Royal Dutch Shell laboratories. Between 1970 and 1973 several students joined the team. Miguel Leiva and Esteban Martina were going to work on a PVT apparatus, although lack of resources redirected their effort to theory, and in particular to the study of the van der Waals model; María Trigueros also started work in the same direction, Francisco Guzmán and Luis Mier y Terán undertook the study of fluid mixtures. Since at the CIM the minimum experimental resources were made available to us, Ricardo Tsumura started the work on PVT that at the time wasn't feasible at the IMP.

In a couple of years the picture had changed completely. We had identified the main specific problems, both basic and practical, and had an informed understanding of them; we had developed an independent view of the fields involved and the first few pieces of research were coming out. Experiments were finally under way at the CIM, where Martín Chávez had started work on ultrasonic absorption and Jean Pierre Monfort had arrived after being a student of Henri Renon in Paris. The work on ultrasonics was possible thanks to a grant from the Fund for Overseas Development and Education, and Monfort's visit was supported by the cooperation program between France and Mexico. Monfort started our experiments with mixtures in colaboration with Guzmán. Our theoretical flank was reinforced by Marcelo Lozada and also by Carlos Arzola, who came from the Universidad de San Marcos at Lima.

During these years the need of securing the assistance of an expert experimental thermodynamicist had become urgent. A most fortunate happening for the success of our endeavours was the arrival of Ian McLure at the IMP by the end of 1973. McLure visited us for six months with the sponsorship of the British Council. His programme had been carefully planned and three new students had been selected and prepared to join him in the laboratory at IMP -which was finally been equiped: Enrique Fernández Fassnacht, Rubén Lazos and Arturo Trejo. Thus, several experiments of interest to the petrochemical industry were started and eventually completed. A close interaction between experimental thermodynamicists in México and McLure's Laboratory in Sheffield has continued to the present.

The story took a different pace by the middle of 1974, and its development was going to be altered. It was time for some teammates to go abroad and pursue different but complementary lines of training. Martina left for MIT where he was going to work with John Deutch in statistical mechanics. Leiva went to the University of Birmingham to do experimental thermodynamics. Guzmán joined McLure in Sheffield. Trigueros went to Berkeley and did work with Bernie Alder. Tsumura went to the NBS Laboratory in Boulder to do low-temperature experimental research. Ponce had left for Paris to work with Henri Renon at the ENSTA, and Guerrero had gone to John Rowlinson, then at the Imperial College, to work on statistical mechanics.

The second important event was the creation of the Universidad Autónoma Metropolitana as an alternative to the traditional higher-education institutions in Mexico. The importance of the birth of the UAM for this story had also to do with timing. Our vision of the field told us that a lot of research had to be done and that some of it was of rather long ranged aims. Nevertheless, the conditions then existing at the IMP made it very difficult to do this type of research; even if it was considered important by international oil companies. Hence, for those of us who had a stronger interest in long term research, the UAM at Iztapalapa offered the opportunity to pursue it. Fortunately, some stayed or were to return to the IMP and play a leading role in its development, although their activities there fall outside the line of this story.

Thus, by the middle of 1974 Mier y Terán, Chávez, Fernández Fassnacht, Dolores Ayala and I joined the UAM at Iztapalapa. Ayala had been my student at the UNAM and became a nice reinforcement of our team. Others joined us later after their stays abroad: Martina, Guzmán and Gustavo Chapela. Chapela had been a student of Tom Leland in Texas and of Rowlinson at the IC, we had met a few years before while I was at the IMP and he at Pemex.

At about this time, we started what was to become a continuing and fruitful relation with Doug Henderson from the IBM lab at San Jose. Newer students and later colleagues at Iztapalapa were Jacqueline Quintana, who started work on mixtures, Sergio Martínez and Ana Laura Benavides. Martínez has been doing simulation work with Chapela and Benavides worked with Martina before playing a role in this story. Still later, Víctor Romero, Leonel Lira and Antonio Muñoz have also contributed as students.

A fruitful contribution to this story was made during a sabbatical leave at the School of Chemical Engineering of Cornell University whose hospitality I enjoyed. There I had the change of profiting from many discussions with Keith Gubbins, Bill Streett and Ben Widom. The visit to Cornell was sponsored by a Fulbright fellowship.

In the last few years, most of the members of the team have matured as independent researchers, and some have moved to other institutions and endeavours. The original goal is still being pursued with their enthusiastic, albeit part-time, support.

II. THE VAN DER WAALS MODEL AND KINETIC THEORY

A. *The model of van der Waals*

Our first job, back in the beginning of the 70's, was connected to the van der Waals (VDW) equation of state. We had been working with several equations of state (EOS), generally called "semi-empirical", which were of wide use in chemical engineering. These equations consist of empirical modifications of VDW equation derived on his thesis of 1873(1), and pretend to improve the quantitative accuracy of the original VDW-EOS. A particularly popular series of semi-empirical equations originate in the Redlich-Kwong equation(2). An initial aim was to find out whether such (or similar) modifications to the VDW-EOS could be understood by physical arguments, so that theoretical improvements could be incorporated. It was soon clear that the formal methods that had led to a rigorous derivation of VDW-EOS(3,4) could not account for the type of behaviour incorporated into the RK and similar equations. Hence, we turned our attention to the original and more approximate derivations of VDW-EOS. Many textbooks contain approximate, qualitative or hand-waving derivations of VDW-EOS(5), and some rely on arguments which are either confusing or wrong(6).

The VDW model provides a way to calculate the thermodynamic properties of a fluid from the binary intermolecular potential u which depends on the relative positions and orientations of two molecules. The essential features that define the van der Waals model (VDW-M) are: 1st, a separation of u in its short-range repulsive part u_r and its attractive part u_a of longer range,

$$u = u_r + u_a \qquad , \tag{1}$$

and 2nd, a corresponding separation of the pressure and other extensive properties in two parts

$$P = P_r + P_a \qquad . \tag{2}$$

Van der Waals also used a particular form for the terms in Eq. (1) and introduced approximations to obtain the terms in Eq. (2). Nevertheless, the latter are additional to the main features of the VDW-M and their improvement leads to revised versions of the original VDW-EOS.

The most relevant consequence of VDW work in 1873$^{(1)}$ was to show how the VDW-M, defined by Eqs. (1) and (2), with approximate expressions for P_r and P_a, explains the existence of the vapour-liquid transition, including its critical point.

In general, there are two broad and different ways to deduce (2) from a given interaction model in (1): The first is the kinetic approach in which one considers the individual molecules, their motions and collisions. The second relies on the statistical mechanical picture developed by Gibbs and is connected with free-volume theory and perturbation methods. The original derivation of van der Waals himself was mostly of a kinetic nature and based on the virial theorem of Clausius$^{(1)}$. Most contemporary textbooks, on the other hand, use the statistical mechanical approach mixed at times with kinetic arguments$^{(5,6)}$.

We will deal with the kinetic and free-volume theories in this section and leave the consideration of perturbation methods for section III.

B. *Molecular collisions and the pressure*

In the original derivation of the VDW-EOS, u_r was approximately represented by the interaction between two hard spheres of diameter σ, whose centers are separated a distance r

$$u_r \cong u_{HS} = \begin{cases} \infty, & r < \sigma \ , \\ 0, & r > \sigma \ . \end{cases} \tag{3}$$

Kinetically, the pressure in a system equals twice the flux of momentum through a surface, in one direction. The effect of the repulsive collisions is to increase such flux; when molecules on either side of the surface collide, momentum will be transferred across and in excess of the (ideal) transport due to the streaming of the particles. But also, the collisions increase the flux of particles through any surface. Then, the net effect of the repulsive forces is to make $P_r > P_{id} > 0$. The original VDW derivation, for a system of N particles at temperature T and occupying a volume V, approximated P_r by

$$P_{HS} \cong \rho kT/(1 - 4b\rho) \quad , \tag{4}$$

where $\rho = N/V$ and $b = \pi\sigma^3/6$ is the volume of one particle. The VDW approximation (4) becomes exact for hard spheres only at low densities, but its qualitative behaviour is correct over the whole fluid range.

In our initial study of the VDW-M with Martina, Leiva and Trigueros$^{(7,8)}$, we obtained kinetically the generalization of the VDW approximation (4). By means of simple but rigorous arguments, we found that

$$P_{HS} = \rho kT/(1 - \eta), \tag{5}$$

where η is the mean distance across which momentum is transferred instantaneously, due to the collisions, per unit length of travel. This quantity can be written in terms of the mean free-path ℓ and of the diameter σ of the particles as

$$\eta = \sigma/(\sigma + \ell) \quad . \tag{6}$$

Eq. (5) was shown to be valid both for the fluid and for the solid. In particular, for a one-dimensional system of hard rods in a box of length L, $\eta = \sigma N/L$ exactly. Substitution of this value in Eq. (5) gives the exact EOS found originally by Herzfeld and Mayer$^{(9)}$, and by Tonks$^{(10)}$, who used more formal arguments.

Another result was to show that, at densities high enough to prevent diffusion of the particles,

$$\eta = \sigma\rho^{1/3} \quad . \tag{7}$$

This result, when introduced in Eq. (5), converts this equation into the Salsburg-Wood EOS from free-volume theory$^{(11)}$. Eqs. (5) and (7) also show that the correct EOS for the solid phase should involve the "free-length" $V^{\frac{1}{3}} - N^{\frac{1}{3}}\sigma$ instead of a free volume.

The EOS (5) can be written in terms of the mean free-path ℓ by substitution of Eq. (6). One thus finds the expression due to Enskog$^{(12)}$

$$Z = P/\rho kT = 1 + \sigma\Omega\rho\ell_0/\ell \quad , \tag{8}$$

where Ω_0 is the cross section of the particles and ℓ_0 is the limiting value of ℓ at zero density. Further, by introducing in Eq. (8) the radial distribution function $g(r)$ at contact $r = \sigma$, we obtained the EOS in the form

$$Z = 1 + \overline{s}\Omega g(\sigma)\rho \ . \tag{9}$$

In this equation, $\overline{s}$ is the mean collision diameter proyected along any direction. In particular, for hard rods, squares and cubes $\overline{s} = \sigma$. For hard disks $\overline{s} = \pi\sigma/4$ and for hard spheres $\overline{s} = 2\sigma/3$. These values of $\overline{s}$ give the correct second virial coefficients and make Eq. (9) identical to that obtained from the virial theorem of Clausius.

These connection between elementary kinetic theory, Enskog's method, Clausius' theorem and the VDW-M, gave a consistent and alternative method to study the EOS. But the fact is that, by the time when these results were presented, the approximations for P_{HS} had been significantly improved and a practically exact EOS of the HS system was known. The contributions were then mostly of academic interest, although the use of kinetic arguments and the mean collision diameter was later going to be proven of importance. (See section IV.C.)

The other contribution to the pressure, arising from the attractive forces, turned out to be more difficult to calculate by kinetic methods. The original VDW approximation for P_a is

$$P_a \cong - \alpha \rho^2 \quad , \tag{10}$$

where α is a constant with the dimensions of energy x volume. It was possible to obtain Eq. (10) kinetically$^{(13)}$, but it was not possible to write its generalization in terms of the collision dynamics. Nevertheless, a kinetic interpretation of P_a through the virial theorem was later obtained and will be described in section IV.C.

C. *Free-volume theory*

An alternative approach for the calculation of P_r is free-volume theory$^{(11)}$ which has been mostly used in models of the solid phase$^{(14)}$. Nevertheless, the VDW approximation in Eq. (4) is commonly justified in terms of the free volume available to a particle, or the corresponding excluded volume. A mean free volume can be defined directly from Eq. (5), but an alternative definition can be made at the level of the free energy of a hard-particle system. Let ΔA be the Helmholtz free energy of the system in excess over the ideal-gas contribution. Then, in a purely repulsive system, the mean free volume per particle V_f is defined as

$$\Delta A/NkT = \ln(V_f/V) \quad , \tag{11}$$

so that V_f equals the Nth root of the free volume available to the N-particle system in its configuration space. Then one simply finds the pressure in terms of the excluded volume $V_e = V - V_f$ to be

$$Z = 1 + \frac{y(\partial X/\partial y)}{1 - X(y)} \qquad , \tag{12}$$

where $X = V_e/V$ is an excluded-volume fraction and $y = b\rho$ is a reduced density called the packing fraction(15). The form of $X(y)$ was found as a power series in the density

$$X(y) = 4y - 3y^2 + \sigma(y^3) \qquad , \tag{13}$$

or could be approximated by assuming that the decrease in X with y is simply proportional to y itself. This assumption leads to the equation for P_{HS} proposed earlier by Scott(16). Again, these results were going to find application later. (See section VI.A).

III. PERTURBATION THEORY AND EQUATION OF STATE

A. *Perturbation methods in liquids*

Even though van der Waals used kinetic arguments to deduce his EOS, the main source of present support and popularity of his model comes from a specific statistical mechanical technique: perturbation theory (PT). The use of perturbation methods for the understanding of the liquid state was well established in the beginning of the 70's. The main points in this development were, on one hand, the proposal of a perturbation expansion by Zwanzig(17) and the extensive work on the hard-sphere system by several methods: computer simulations(18,19), virial expansions(20), scaled-particle theory(21), and integral equations(22,23). On the other hand, the work of Barker and Henderson (BH)(24) which was the first succesful theory of the liquid state. The reader may consult the abundant review literature on the subject for a detailed account(25-27).

The main ideas of the PT of liquids conform to the VDW model as stated in the previous section. Perturbation methods thus give to it a formal content and allow concrete calculations of the model which can be systematically improved by statistical mechanical methods. The application of PT to realistic fluids has been most succesful for simple fluids, whose intermolecular potential u(r) depends only on the distance r between two molecules. The extension to the more complicated molecular fluids is also possible(28), but for simplicity we will restrict ourselves to the case of simple fluids. These perturbation methods consist of three essential steps:

1) A separation of the interaction potential u(r) in a repulsive and an attractive part as in Eq. (1).
2) A first perturbation expansion of the properties of the system with potential u_r about those of the HS system, which is used as reference.
3) A second expansion to incorporate the attractive forces in which u_r is the reference and u_a is the perturbation.

These steps separate the thermodynamic properties of the system in the same spirit of the VDW-M, Eq. (2). Thus, the excess Helmholtz free-energy per particle becomes separated in a repulsive and an attractive part

$$\Delta A/NkT = a_r + a_a \quad . \tag{14}$$

Due to step 2), one finds

$$a_r(\rho,T) = a_{HS}(\rho^*) + a'(\rho^*,T;[u_r]) + \dots , \tag{15}$$

where $\rho^* = \rho\sigma^3$ is the reduced density and kTa_{HS} is the excess free energy of the HS system. Due to step 3), the attractive energy is expanded in terms of the inverse temperature as

$$a_a(\rho,T) = a_1(\rho^*)/T^* + a_2(\rho^*)/T^{*2} + a_3(\rho^*)/T^{*3} + \dots , \tag{16}$$

where $T^* = kT/\varepsilon$ and ε is the depth of the attractive well of u(r).

Actually, there are several ways in which any of these steps can be implemented. The reader is referred to the literature(25-27) for details, but a few comments are in order:

- There are several ways to take steps 1) and 2), and therefore the perturbation terms a',... in Eq. (15) can take different forms.
- The perturbation expansions in 2) and 3) are of a very different

nature: step 2) has the effect of softening the HS potential, whereas step 3) incorporates the attractive forces as a small effect and its first-order term is the mean field

$$a_1 = \langle u_a \rangle_{HS} = \frac{1}{2\varepsilon}\rho\int d^3r \; g_{HS}(r;\rho^*)u_a(r) \quad , \tag{17}$$

where $g_{HS}(r)$ is the radial distribution function of the reference HS fluid.

- Expansions 2) and 3) also differ in their convergence properties.

As a matter of fact, expansion 2) needs a definition of the diameter σ of the HS used as reference. This is commonly accomplished by requiring that the 1st-order correction term to the free energy, a' in Eq. (15), vanishes$^{(25)}$. Thus, neglect of the 2nd and higher-order terms makes

$$a_r(\rho,T) \cong a_{HS}(\rho^*) \quad , \tag{18}$$

where the HS diameter σ appears in $\rho^* = \rho\sigma^3$ and is defined by the solution to the equation

$$a'(\rho,T;\sigma,[u_r]) = 0 \quad . \tag{19}$$

This equation makes the HS diameter dependent on the state (ρ,T) and (functionally) on the potential $u_r(r)$. In the BH theory, σ depends only on T and Eq. (19) gives σ explicitly$^{(24)}$. The Weeks-Chandler-Andersen theory (WCA) gives σ implicitly as a function of both ρ and $T^{(29)}$.

It turns out that, for a realistic u_r, the definition of σ in Eq. (19) makes the expansion in Eq. (15) highly convergent. Thus, Eq. (18) becomes a very good approximation and it is not necessary to go to higher orders in the expansion for most practical purposes.

For realistic potentials truncation of the second expansion, Eq. (16), after the 1st-order mean-field term, a_1, is not enough to give accurately the thermodynamic properties bellow the critical temperature.

A brief statement must be added about the methods that combine perturbation and variational methods$^{(30,31)}$. These methods establish the first-order PT approximation as an upper bound to the free energy of the repulsive system and determine the "best" value of the HS diameter σ by minimizing the perturbed free energy, Eq. (15) with respect to σ. These procedure gives an implicit definition of σ which may be expressed in a form similar to Eq. (19), and the values of $\sigma(\rho,T)$ behave in general as those obtained from the BH and WCA perturbation expansions.

B. *Perturbation methods and the VDW model*

The perturbation methods outlined in the last section allow a systematic improvement of the VDW-EOS. This possibility has given rise to a whole series of "augmented", "corrected" or "generalized" VDW theories theories$^{(32-34)}$. All these developments have several common characteristics:

1) They start by assuming a particular form of the intermolecular potential u(r) as, *e.g.*, the 12-6 Lennard-Jones potential.
2) They separate this potential as in Eq. (1), which is usually done at the distance r_m where u(r) is minimum; this separation has been shown to produce a more convergent expansion in Eq. (10)$^{(26,27)}$.
3) They calculate the effective diameter by Eq. (19) or its equivalent, which in the more convergent WCA theory$^{(29)}$ makes σ to depend on temperature and density.
4) They use an accurate expression for the HS free-energy in Eq. (15) and neglect higher-order terms.
5) They calculate the mean-field term a_1, given by Eq. (17).
6) In many cases, these methods calculate the second-order term a_2 of expansion (16). Although for some model systems, like the SW potential, a_3 and a_4 have been calculated$^{(35)}$.

Calculation of the thermodynamic properties of simple fluids by means of these corrected VDW theories has an eror of only a few percent. To reach this accuracy, it is nevertheless necessary either to use effective binary potentials, which depend on the thermodynamic state, or to take into account the non-additive three-body forces$^{(36,37)}$. Furthermore, these applications of the perturbation methods do not really produce true equations of state because it has not been possible to obtain a_1, Eq. (17), analytically for a given potential u_a; to incorporate analytic expressions for the second order term a_2, and for the effect of the three-body forces is even more difficult. Thus, these methods produce tables of thermodynamic properties instead of equations, although sometimes they are referred to with the latter name.

C. *Exact deduction of the VDW-EOS*

A very important development concerning the VDW model was the work of van Kampen(38), Kac *et al.*(3) and Lebowitz and Penrose(4). They have shown how to obtain rigorously and exactly the (modified) VDW-EOS for a general class of potentials of the type referred to by Eq. (1). For a HS core their work leads rigorously to

$$\Delta A(\rho,T)/NkT = a_{HS}(\rho^*) - \alpha\,\rho \quad , \tag{20}$$

where a_{HS} is the exact HS excess free-energy per particle. From this relation, Eq. (10) follows immediately. Kac *et al.* and Lebowitz and Penrose found that Eq. (20) is exact for a potential consisting of a HS repulsive part plus an attractive part which is infinitely weak and long ranged. This attractive potential was represented by the Kac (or Yukawa) form

$$u_K(r) = -C\gamma\exp(-\gamma r)/r \tag{21}$$

in the limit when the inverse range $\gamma \rightarrow 0$. Lebowitz and Penrose(4) further showed how to obtain rigorously the vapour-liquid equilibrium line, including the Maxwell construction, in the same limit.

Nevertheless, a word of caution is in order about this point: Eq. (20) is exact for the Kac potential (21) in the limit just mentioned, but this is not the actual potential of interaction between real molecules, *i.e.* there is no real fluid for which Eq. (20) is accurate over the whole fluid region.

It is of historical interest that Boltzmann guessed this result around the year 1900(39). In a letter to van der Waals, Boltzmann argued that for the VDW-EOS to be correct, the intermolecular forces should not be as van der Waals proposed, but that their attractive part had to be infinitely weak and long ranged! He was proven to be right 65 years later. Actually, van der Waals argued back that he thought the real intermolecular potential had to be of finite range and depth. He was also right!

D. *The VDW-EOS and real fluids*

From the discussion in the last sections it is clear that the modified VDW-EOS given in Eq. (20) is an approximation to the behaviour of real fluids. Actually, if an improved HS-EOS is used for the first term of Eq. (20), instead of the original VDW approximation leading to Eq. (4), the resulting EOS is in good overall agreement with experimental results for argon when the VDW parameters b and α are chosen appropriately (Longuet-Higgins and Widom$^{(32)}$). But then the following question arises: are there any conditions where the improved VDW-EOS becomes quantitatively exact for real fluids? The answer to this question was considered in a paper with Arzola$^{(40)}$.

The extensive work with perturbation methods has shown that the repulsive part a_r can accurately by represented by a HS term with suitably chosen diameter σ, hence, the question above really concerns the validity of the VDW approximation for the attractive part, Eq. (10), equivalent to Eq. (20). In order to test this approximation, one can first write the repulsive contribution by means of the highly accurate approximation in (18), so that the full excess free energy in Eq. (14) becomes

$$\Delta A/NkT = a_{HS}(\rho\sigma^3) + a_a(\rho,T) \tag{22}$$

and then ask about the form of the attractive energy $a_a(\rho,T)$. When is a_a proportional to ρ? Of course, perturbation theory gives a way to answer this question by explicitly allowing the calculation of a_a by the series in Eq. (16). But this can only be done if the form of the intermolecular potential is known. However, such is not the case for the great mayority of real substances.

When the potential u(r) is unknown, Eq. (19) cannot be used and one needs to determine the effective diameter σ from the knowledge of the thermodynamic properties of a substance. The problem of determining the parameters of an EOS from purely thermodynamic data is an old question confronted in practical cases by chemical engineers. The two most common answers are: obtain σ and other parameters by fitting the EOS to a wide set of experimental data of the substance, or alternatively, obtain the parameters from the experimental results at a few selected points, *e.g.*, the critical or the triple points. In order to test the modified VDW-EOS none of these methods is useful. For, an empirical fit will never decide a question of validity, and one cannot use information about a particular point if the validity of the EOS at that point is in doubt. Moreover, the VDW approximation is certainly wrong at the critical point, which is the most popular in fitting. In conclusion, we had to look for a way in which both the value of σ could be found and the validity of the VDW approximation (10), could be tested. The way to do this was inspired by the perturbation results.

The first point was to look at the high temperature region, for in that case the inverse temperature expansion, Eq. (16), gives

$$a_a(\rho,T) \xrightarrow[T \longrightarrow \infty]{} a_1(\rho)/T^* \qquad (23)$$

The next point is then to consider when is a_1, given by Eq. (17) proportional to the density, as in the VDW equation (20). The integral in Eq. (17) is roughly proportional to the number of particles within the attractive well of a given one. Since for real fluids the potential u_a is of rather short range, that number will be constant at high densities.

With those elements, it was possible to look at the high density part of the high-temperature isotherms, and see if there exists a value of σ that makes $a_a(\rho, T)$ constant in Eq. (22) when the left-hand side is obtained from experimental results. The answer was affirmative(40): the VDW approximation for A becomes exact at high temperatures and densities, and the values of σ found by this "bootstrap" method were in rough agreement with the sizes of the molecules as obtained by molecular and statistical mechanical methods. The substance used initially in these studies was argon$^{(40)}$ and later other noble gases$^{(41)}$.

IV. THE VDW MODEL AND REAL FLUIDS

A. *Intermolecular forces and the inverse problem*

Most knowledge and insight about classical fluids, gained by statistical mechanics, has been achieved by assuming particular forms of the intermolecular potential. These potential models have been of enormous importance in statistical mechanics and have led to discover which features of real intermolecular forces are most relevant in the thermodynamic behaviour of real fluids. Nevertheless, in order to calculate accurately the thermodynamic properties of real fluids, it is necessary to start with accurate intermolecular potentials. But, since these are presently unknown for the vast majority of substances, one has to look for alternative approaches. Is it possible to construct an EOS of a real substance that is based on statistical mechanics but does not require the intermolecular forces to be known? The affirmative answer is well exemplified by the virial EOS for gases: it can be constructed from purely thermodynamic measurements, has a wide applicability and is theoretically derived from statistical mechanics$^{(42)}$. This question is closely related to the so called inverse problem: Can we learn anything about the molecules and their interactions by an appropriate analysis of thermodynamic data?

A possible approach to construct a theoretical EOS(TEOS) for dense real fluids is found in perturbation methods themselves. The expansion used to express the properties of the repulsive system u_r in terms of the HS reference, Eq. (15), actually allows to write an EOS: precisely the EOS of a HS system with a diameter σ that depends on temperature and (slightly) on density. All systems with purely repulsive potentials $u_r(r)$ will have an approximate EOS, Eq. (18), of the same form; the detailed differences in $u_r(r)$ between systems give rise to different dependences of σ with T and ρ. So far so good. However, the treatment of the attractive part in Eq. (16) is quite different: it does not lead to a thermodynamic equation that involves the variables T and ρ, and some parameters. Even the simpler first-order term, Eq. (17), does not determine the thermodynamic parameters which are relevant to describe the effect of the intermolecular attractions.

Hence, to obtain a TEOS it was essential to develop a perturbation theory dealing with the attractive interactions in the same manner as the repulsive forces are treated in the usual theories. Such a theory should provide an approximate but closed-form EOS and determine which parameters are adequate to describe the effect of the attractive forces, in the manner that the diameter $\sigma(\rho,T)$ does for the intermolecular repulsion. This development is described in the next section.

B. *The square-well perturbation method*

The success of perturbation methods based on the HS model is due to three factors: the great similarity between the effects of the HS interaction and those of real repulsive forces, the predominance of repulsive effects on the structure of the liquid, and the simplicity of the HS potential. In order to construct a theory with similar virtues and incorporating the attractive forces, one needs as reference system a model potential that keeps the HS repulsion additioned by the simplest type of attraction. An obvious choice is the square-well (SW) potential

$$u_{SW}(r) = \begin{cases} \infty, & r < \sigma \quad ; \\ -\varepsilon; & \sigma < r < R \quad , \\ 0, & R < r \quad . \end{cases} \tag{24}$$

This potential was used in the work with the Lonngi$^{(43)}$ to extend the perturbation methods of BH$^{(24)}$ and WCA$^{(29)}$ so as to include an attractive potential in the reference system. The expansion obtained for the total excess free energy per particle, $\Delta a(\rho,T)$, which takes the place of both Eqs. (15) and (16), is

$$\Delta a(\rho,T) = a_{SW}(\rho^*, T^*, \lambda) + a'_r + a'_a + \ldots \tag{25}$$

where a_{SW} is the excess free energy of the SW system, $\lambda = R/\sigma$ and the perturbation terms a'_r and a'_a involve the SW distribution functions and the repulsive and attractive parts of the potential u(r), respectively. In the same spirit of the HS perturbation methods, the two SW parameters σ and R are chosen by requiring vanishing first-order terms:

$$a'_r(\rho,T;\sigma,R,[u_r]) = 0 \quad ,$$
$$a'_a(\rho,T;\sigma,R,[u_a]) = 0 \quad ; \qquad (26)$$

the third parameter was chosen equal to the depth of the well of u(r). With this definition of the SW parameters, and neglecting the second and higher-order terms, Eq. (25) becomes

$$\Delta a(\rho,T) \cong a_{SW}(\rho^*,T^*,\lambda). \qquad (27)$$

In order to test the first-order approximation in (27) with σ and R given by Eqs. (26), we applied this expansion to the Lennard-Jones 12-6 system$^{(43)}$, which is quite realistic and whose thermodynamic properties are rather well known.

The results found show that the 1st-order approximation in (27) is very convergent and in all respects competitive with the expansions based on the pure HS$^{(43)}$. In particular, Eqs. (26) uncouple in the low density limit and one can solve them explicitly for σ and R. The results depend on whether the method used is the "blip" expansion$^{(29)}$ or the "α - expansion"$^{(24)}$. In the latter case one recovers, at $\rho = 0$, the BH expression for σ deduced from Eq. (19) and the corresponding generalization for the mean range R$^{(43)}$. In the former case one gets

$$\sigma_0^3 = 3\int_0^{r_m} \{1 - \exp[-\beta(\varepsilon + u(z))]\}\, z^2 dz \quad ,$$
$$R_0^3 = r_m^3 + 3(e^{\beta\varepsilon} - 1)^{-1} \int_{r_m}^{\infty} \{\exp[-\beta u(z)] - 1\}\, z^2 dz \quad ; \qquad (28)$$

where σ_0 and R_0 are the low density values of σ and R, respectively. The behaviour of $\sigma(\rho,T)$ was also shown to be similar to that found in the WCA theory$^{(29)}$ and, in particular, $\sigma_0 = \sigma_{WCA}$ $(\rho = 0)$.

C. *Effective parameters and kinetic theory*

The behaviour of σ and R with temperature is quite simple for a realistic u(r) like the Lennard-Jones 12-6 potential(43): σ decreases monotonically with T, starting from the value $\sigma = r_m$ at $T = 0$; on the other hand, $R = r_m$ at $T = 0$ and therefrom increases monotonically with T reaching a finite value when $T \longrightarrow \infty$.

In particular, the decrease of σ with T has an intuitive qualitative appeal: soft-core molecules appear to be smaller at higher temperatures because the larger momentum will reduce the distance of closest approach on a collision. This qualitative fact suggested that the kinetic approach described in section II.B could be extended to deal with soft molecules. This extension was rigorously proven with de Lonngi in a very simple way(44). If s is the collision diameter for two molecules which collide with kinetic energy E, the probability density p(s) of a given s is easily obtained from the Maxwell distribution for E, p(E). One immediately finds that

$$\langle s\rangle(\rho = 0) = \int_0^{r_m} ds \, \{1 - \exp[-\beta u(s)]\} \quad , \tag{29}$$

where the average $\langle\rangle$ is taken with respect to E. But the right hand side of Eq. (29) is just the expression for the effective diameter in the BH theory as obtained from Eq. (19), *i.e.*,

$$\sigma_{BH}(T) = \langle s\rangle(T, \rho = 0) \quad . \tag{30}$$

Later we also found the connection between σ_0, Eq. (28), which is identical to $\sigma_{WCA}(\rho = 0)$, and an average of the collision diameter(43):

$$\sigma_0^3(T) = \langle s^3\rangle(T, \rho = 0) = \sigma^3{}_{WCA}(T, \rho = 0) \quad . \tag{31}$$

Also, we showed that the effective range R, Eq. (28), is equal to a mean range

$$R_0^3(T) = \langle h^3\rangle(T, \rho = 0) \ , \tag{32}$$

where the range h is the maximum distance of separation between to bound particles.

Eqs. (29) to (32) establish a connection between two approaches and gibe a new insight into the parameters used by the perturbation theories. This also means that the low-density values σ_0 and R_0 that enter into the EOS of a simple fluid, Eq. (27), are respectively equal to the mean collision diameter and the mean attractive range.

The rigorous extension of Eqs. (31) and (32) to finite ρ has not been completed yet. It has been shown that this extension relies on the use of collision frequencies in the manner of Enskog's theory(12) so as to generalize Eq. (9) for an arbitrary potential(49). The question is being investigated by means of the molecular dynamics method as applied to discontinuous potentials(50). Nevertheless, by assuming the validity of Eqs. (31) and (32) at any density it has been possible to interpret kinetically the behaviour of $\sigma(\rho,T)$ and of $R(\rho,T)$ for a variety of systems, both spherically symmetric and asymmetric(48,49,51). The soundness of these interpretations is in support of the assumption.

V. CORRESPONDING STATES AND SYSTEMS

A. *Generalized corresponding states and systems*

A look at Eq. (27) is enough to realize that the EOS of all simple fluids can be written (approximately) in the same universal form if the appropriate reference systems and reduced variables are used. This fact recalls the Principle of Corresponding States(45) for classical fluids. Two substances S and S' are said to follow the PCS when the thermodynamic properties of S at any state (ρ,T) become equal to those of S' at another state (ρ', T') such that the scale ratios ρ/ρ' and T/T' are constant, independent of the state. Two such states are then said to correspond to each other. The two substances follow the PCS if their intermolecular potentials u(r) and u'(r) differ only by constant scale factors of distance and energy. Such potentials, or substances, are also said to be conformal. The fact that there are sets of real substances which follow the PCS stems from the scaling similarity of their intermolecular potentials within each set(45,46,49). These sets may be called conformal sets.

Hence, all substances within a given conformal set have the same EOS if written in terms of variables reduced with the appropriate constant scaling factors. One only needs to know the EOS of one substance of the set and the appropriate changes of scale, to obtain the EOS of all the other substances in that set. A limit in the applicability of the PCS to construct EOS is the exclusive character of the notion of conformality: two substances are either conformal or not, there is no room for differences in degree; it is impossible to incorporate the effect of a deviation from conformality.

Actually, the perturbation methods allow to tackle the last problem, although approximately. The BH method of softening the hard core$^{(24)}$ and the "blip" expansion of Weeks *et al.*$^{(29)}$, relate the thermodynamic properties of two non conformal potentials: the HS reference and the soft $u_r(r)$ -Eq. (18)-. The extension of these ideas to incorporate the attractive u_a in a similar way allows the SWPT of the Lonngi and del Río$^{(43)}$ to relate the full u(r) to its non-conformal reference u_{SW} in Eq. (27). This is done by a standard statistical method which requires u(r) and the distribution functions of the SW reference to be known, and is done in an approximate way.

In order to overcome the limitations of the PCS to conformal substances, a generalization of the PCS was presented several years ago$^{(47)}$. In its generalized version, the PCS again changes the scale of the thermodynamic variables to relate corresponding states, but now the scale factors depend in general on the state variables themselves.

The generalized PCS agrees with the SWPT result, Eq. (27), in one important aspect: the EOS of all simple substances takes the same form in terms of the state-dependent reduced variables, although the SWPT relation is only an approximation and not an equality. Nevertheless, there are two great differences between the GPCS and the SWPT: 1) the reference in the latter is not a real substance, but a model one, and 2) both systems S and S_{SW} are not in "corresponding" states but in the same state (ρ,T).

Based on these considerations, a modification of the GPCS, called "method of corresponding systems" was proposed and applied initially to systems with purely repulsive potentials$^{(46)}$. In this simpler case, the reference is the HS system. Instead of the approximate perturbation relation (18), one imposes the equality between the properties of the system S of interest and the reference S_{HS}:

$$\Delta a(\rho,T) = a_{HS}(\rho^*) \quad . \tag{33}$$

The MCS expresses the EOS of S as the HS-EOS with an appropriate $\sigma = \sigma(\rho,T)$. The latter can be obtained in either of two ways:

1) When the potential u() of S is unknown but its thermodynamic properties have been measured or calculated by computer simulation, σ is obtained from Eq. (33) for any given ρ and T.
2) When u is known, approximate values of $\sigma(\rho,T)$ can be obtained by perturbation methods, Eq. (18).

It must be added at this point, that both the perturbation methods and the MCS can be applied to other thermodynamic properties besides the Helmholtz free energy. Thus, expressions equivalent to (18) and (33) can be written for the pressure, the compressibility, etc. Each choice of thermodynamic function leads to different definitions of the effective diameter σ.

In the MCS all the particularities of a substance are incorporated into the functional dependence of $\sigma(\rho,T)$. Thus, since no universal or simple form of $\sigma(\rho,T)$ has been proposed, a complicated behaviour of $\sigma(\rho,T)$ would seriously limit the applicability of the MCS. Fortunately it was found that this is not the case. In particular, for a wide sample of repulsive potentials, including non-spherical ones, it was found that $\sigma(\rho,T)$ can be written in a virial expansion(48)

$$\sigma(\rho,T) = \sigma_0(T) + \sigma_1(T)\rho + \dots \tag{34}$$

through the complete fluid range up to the solidification line. It was found that the expansion (34) is highly convergent: it is only necessary to keep three or four terms in order to achieve an accuracy similar to that of present day computer simulations(48,49). This is an important point; it means that one only needs a few selected data at each temperature in order to find $\sigma(\rho,T)$ in the whole density range.

The MCS was also applied to non-spherical particles, *e.g.* hard spherocylinders and dumbells(48). It was found that the effective diameter is temperature independent, because the particles are hard, but that their eccentricity makes σ to be density dependent: the increase in orientational ordering of the particles at high densities makes the effective diameter σ to be smaller than at low density. This fact is easily understood by appealing to the kinetic expression for σ, Eq. (30: the aligment of the molecules in dense states increases the collision rate for smaller diameters.

B. *Corresponding systems and real substances*

The MCS was further developed to cover real systems by using as a reference the same SW system as in the SWPT(49). With the SW reference, the three parameters ε, σ and R have to be determined. This has to be done in such a way that the phase diagram of both systems S and S_{SW} are mapped into each other so that all states along phase lines and critical points coincide. The possibility of using references different from the SW was also considered and judged at this time impractical(49).

In order to test the applicability of the MCS, together with Fernández Fassnacht we applied it to a set of monoatomic and molecular fluids(51). The correspondence used in this work identifies the orthobaric states of the substance to those of the SW system. The effective SW parameters are chosen in the following way:

1) The depth ε is taken constant, as in the perturbation expansion, and its value obtained from the compressibility factor $Z_{SW} = PV/NkT$ of S_{SW} at the critical point.
2) The value of the reduced range $\lambda = R/\sigma$ at each orthobaric state was found from the equality of the compressibility factors

$$Z(T^*) = Z_{SW}(T^*,\lambda) \qquad . \qquad (35)$$

3) The mean diameter σ was then obtained from the orthobaric SW density

$$\sigma^3(T) = \rho^*(T^*,\lambda)/\rho(T) \quad . \qquad (36$$

Results were obtained for A, N_2, CH_4, CF_4, CF_3Cl, CF_2Cl, $CFCl_3$, CCl_4 and CO_2. The test of the MCS proved to be succesful, showing in particular the following points:

a) The method is feasible, *i.e.*, Eqs. (34) and (35) have real solutions for σ and λ.

b) The behaviour of σ and R with ρ and T, agree qualitatively with all predictions based on the HS and SW perturbation methods and with their kinetic interpretation. The exception are the second derivatives of σ and R with ρ, which are of opposite sign from the SWPT calculations.

c) The present knowledge of the SW reference fluid is sufficient to make the MCS work.

d) A conformality between different substances was exhibited explicitly in all cases where it was expected (*e.g.* argon and methane). Also, a partial conformality, *i.e.* between the repulsive parts of the potential, was found for the CF_4 family. This indicates a similarity of their repulsive forces which is commonly hidden by the non-conformality of their attractive potentials.

e) The EOS takes the generalized VDW form, as Eq. (14).

C. *Development of the SW EOS*

In both SWPT and MCS one needs the knowledge of the properties of the SW system. The MCS relies on the thermodynamic properties, whereas the SWPT also needs the radial distribution function $g_{SW}(r)$. The sources of information about S_{SW} are of the same types as for HS: integral equations for the distribution functions(52), perturbation methods(53), and Monte Carlo or molecular dynamics simulations(54,35). There is no accurate analytic theory for the SW g(r) and the best numerical results are provided by simulations(54,35). Thus, de Lonngi and del Rio proposed an analytic and empirical representation of $g_{SW}(r)$ based on the simulation results(55,56). This was the representation used in the SWPT(43).

The thermodynamic properties of S_{SW} deserve some discussion. The

SW-EOS can be written by means of a high-temperature perturbation expansion, similar to that in Eqs. (14-16), in terms of a HS reference, to obtain an EOS of the VDW type:

$$-a_{SW} = a_{HS}(\rho^*) + a_a(\rho^*, T^*, \lambda) \qquad ; \qquad (37)$$

where again a_a is expanded in terms of the inverse temperature by Eq. (16). Henderson *et al.*(54) calculated the first two terms in this expansion, a_1 and a_2, by the Monte Carlo method for SW systems for several values of λ between 1.125 and 2. Fernández Fassnacht used these results to obtain the vapour-liquid equilibrium including the position of the critical point(57). These orthobaric data were then used in the application of the MCS to real fluids(51,57). For Eq. (35) to have a solution at the critical point, $Z_c(\lambda)$ should take the value $Z_c = 0.29$, characteristic of real simple fluids. The exact result for $\lambda = 1.5$ gives $Z_c(1.5) = 0.29$, which is an encouraging value(35), but the second-order approximation to a_a gives larger values of Z_c for all λ(54,57). This limitation prevents the present use of the MCS close to the critical point(51,57). In order to remove this limitation, and also to obtain an analytic expression for a_{SW}, we have developed theories in the long ($\lambda \gg 1$) and short range ($\lambda \cong 1$) limiting cases.

The long-range case was first analized by Ponce and Renon(58). The first-order term for the SW system is

$$a_1 = -2\pi\rho \int_0^R dr\ r^2 g_{HS}(r,\rho^*) \qquad , \qquad (38)$$

which becomes, when $\lambda \gg 1$,

$$a_1 = -\frac{2\pi\rho}{3} R^3 - \frac{1}{2\rho}\left[K_{HS}(\rho^*) - 1\right] + 2\pi\rho\, B(\rho^*, \lambda) \qquad , \qquad (39)$$

with

$$K_{HS}(\rho^*) = \beta^{-1}(\partial\rho/\partial p) \qquad ,$$

where $B(\rho^*, \lambda) \rightarrow 0$ when $\lambda \rightarrow \infty$. One notices that the first term in

Eq. (39) is just the VDW term with $\alpha = R^3\varepsilon$. The second term was the one calculated by Ponce and Renon$^{(58)}$. The long range approximation has recently being extended to the higher-order terms a_2 and a_3 by Benavides to provide close-form expressions and the accuracy of the approximation is presently being tested$^{(59)}$.

The short-range approximation, $\lambda - 1 \rightarrow 0$, has been studied in collaboration with Lira$^{(60)}$ by means of standard perturbation techniques. One obtains again analytic expressions in this limit, in terms of powers of $\lambda - 1$. These results are also being tested and used to predict the vapour-liquid equilibrium of the SW fluid in this limit.

A further extension of the study of the reference system involves the simultaneous use of a SW attraction, introduced to model the dispersion forces, plus multipole terms introduced to model the electrostatic interactions. In this way one finds the effect of the non conformality of the dipolar and quadrupolar terms on the vapour-liquid equilibrium$^{(59)}$.

VI. EOS, FLUID MIXTURES AND SOLUTIONS

A. *Solution theories and the VDW model*

The problem of dense fluid mixtures differs at high and at low pressures. In the latter case, it is very convenient to separate the contributions to the chemical potential μ_α of the α-th species in a liquid phase in several parts. In a first step, μ_α is written in terms of $\mu^0{}_\alpha$, the chemical potential of the same species as a pure fluid at the same P and T as the mixture,

$$\mu_\alpha(P,T,\{x_\alpha\}) = \mu^0{}_\alpha(P,T) + \delta\mu_\alpha(P,T, \{x_\alpha\}) \qquad , \tag{40}$$

where the composition of the mixture is given by the mole fractions $x_\alpha = n_\alpha/n$, n is the total number of moles, and $\delta\mu_\alpha$ is measures the change in μ_α due to the fact that the α species is not in its pure state but in a mixture. At low pressures, $P \ll P_c$: the critical pressure, $u^0{}_\alpha$ is readily accesible to experimental determination and thus $\delta u^0{}_\alpha$ is the property to be predicted. This is usually done by means of solution models.

If $X(P,T,\{n_\alpha\})$ is an extensive thermodynamic property of the system, one defines the function of mixing $\Delta_m X$ by

$$\Delta_m X(P,T,\{n_\alpha\}) = X(P,T,\{n_\alpha\}) - \sum_\alpha X^0_\alpha(P,T,n_\alpha) \quad , \tag{41}$$

where the second term on the right-hand side is the value of X for the system before mixing X^0_α is calculated for the α species in its pure state. The goal of a solution theory is to predict the Gibbs energy of mixing $\Delta_m G$ by assuming a molecular model. Since the mixing process in Eq. (41) is commonly defined at constant P and T, one can write $\Delta_m G$ in terms of the entropy and enthalpy of mixing, $\Delta_m S$ and $\Delta_m H$, by

$$\Delta_m G = \Delta_m H - T\Delta_m S \quad . \tag{42}$$

These quantities may be obtained from an equation of state for the mixture, or from a specific model of the solution.

At high pressures, on the other hand, Eq. (40) is not too meaningful and the emphasis is made in obtaining an EOS for the mixture, and in deducing from it all the relevant quantities. Perhaps the strongest test of an EOS for mixtures is to ask whether it predicts correctly the phase-equilibrium phenomena. These are of great theoretical interest and also of wide practical importance(56). In all cases, of low or high pressures and of solution models or EOS, most actual applications are still done by means of empirical(61,62) or semi-empirical(63,64) methods.

On the theoretical side, the VDW model has been used both to obtain the functions of mixing and to construct EOS for the mixture. We will mostly refer here to the low-pressure case, but we must mention that the VDW model and EOS are able to predict and classify correctly most phase-equilibrum phenomena, as was shown by Scott and van Konynenburg in their fundamental work(65). On the low-pressure regime, since the work of van Laar the original VDW-EOS was used to obtain $\delta\mu_\alpha$ (or its equivalent "activity coefficient") from which the mixing Gibbs energy $\Delta_m G$ can be derived(66).

Our first work in this direction, together with Guzmán and Mier y Terán, was to obtain the properties of mixing from a generalized

VDW-EOS(67,69). In this work we made use of the VDW one-fluid-theory (OFT), in which the properties of the mixture are represented by those of a (hypothetical) pure fluid, whose characteristic parameters are written in terms of the interaction parameters of the components by means of "mixing rules"(70).

In all mixing processes, one may separate the contribution from the "ideal mixing". In the mixing of ideal gases one finds

$$\Delta_m^{id} g = RT \sum_\alpha x_\alpha \ln x_\alpha \quad , \tag{43}$$

where $g = G/n$ is the molar Gibbs energy. Hence, one defines an "excess" function of mixing by substracting the ideal contribution in Eq. (43):

$$g^\varepsilon = \Delta_m g - \Delta_m^{id} g \quad , \tag{44}$$

and similarly for the other mixing properties. To introduce the improved VDW-EOS, Eq. (14), to the mixture problem, one uses the expression involving the free volume, Eq. (11), to define a free-volume fraction ϕ_α for the α species as

$$\phi_\alpha = V_f^\alpha / V_f \quad , \tag{45}$$

where V_f is the free volume of one particle in the mixture and V_f^α is the free volume of a particle of type α before mixing. One also needs the VDW attractive energies per mole for the α species

$$\alpha_\alpha = N_4 v_\alpha a \quad . \tag{46}$$

In Eq. (46), v_α is the molar volume of the α species and a is defined in Eq. (14) written for the same component. In the original VDW approximation, α_α is a constant. The resulting excess Gibbs energy of mixing is then(69)

$$g^\varepsilon = \sum_\alpha x_\alpha [RT \ln(\phi_\alpha / x_\alpha) + P(v - v_\alpha) - \alpha/v + \alpha_\alpha / v_\alpha] \quad , \tag{47}$$

from which s^ε and h^ε are readily calculated and involve the changes of the

EOS effective parameters, the diameters σ and VDW energies α_α of the α component, with temperature:

$$l_\alpha = -[\partial \ln\sigma^3_\alpha/\partial \ln T] \quad , \tag{48}$$

and

$$m = -[\partial \ln\alpha_\alpha/\partial \ln T] \quad . \tag{49}$$

Most solution models, since they are used at low pressures, assume that $P = 0$. A particular type of models describe the properties of the so-called athermal mixtures, for which $h^\varepsilon = 0$. In this case, the important quantity becomes s^ε. Imposing these conditions on Eq. (47), and assuming the VDW approximation for the free volumes, given by the first term in Eq. (13), we found the following set of results, which are equivalent to each other within the assumptions$^{(67-69)}$:

$$s^\varepsilon = -R\sum_\alpha x_\alpha \ln[(v_\alpha - 4b_\alpha)/(v - 4b)] \quad , \tag{50}$$

$$= -R\sum_\alpha x_\alpha \ln(v_\alpha/v) \quad , \tag{51}$$

$$= -R\sum_\alpha x_\alpha \ln(b_\alpha/b) \quad . \tag{52}$$

These equations are identical to those obtained by well-known models for athermal solutions: Eq. (50) is the result of Hildebrand$^{(71)}$, and Eqs. (51) and (52) are those of the models of Flory$^{(72)}$, Guggenheim$^{(73)}$ and Huggins$^{(74)}$. Hence, the generalized VDW result expressed by Eq. (47) includes these models as particular cases.

A second result of the work with Guzmán and Mier y Terán was to show that Eq. (47) also includes as a particular case the model of Scatchard and Hildebrand for the so-called "regular" solutions. These are mixtures for which the excess entropy of mixing s^ε vanishes and the important quantity becomes h^ε. Again, letting $P = 0$ and $s^\varepsilon = 0$, and assuming the original VDW approximation α = constant, we found that

$$h^{\varepsilon} = - v\left[(\sum_{\alpha} \delta_{\alpha}\phi_{\alpha})^2 - \sum_{\alpha} \delta^2{}_{\alpha}\phi_{\alpha}\right] \quad , \tag{53}$$

where the "solubility parameters" δ_{α} are given by

$$\delta_{\alpha}^2 = - (1 + m_{\alpha} - 1_{\alpha})\alpha_{\alpha}/v_{\alpha} \quad . \tag{54}$$

Then, if the excess volume of mixing $V^{\varepsilon} = 0$, as is implied by the solution being regular, one gets from (53) the Scatchard-Hildebrand result$^{(75)}$.

The generalization of the SH theory was used with Lozada and Monfort to obtain values of the solubility parameters which are consistent with measurements both of the EOS, through Eq. (54), and of the heat of mixing h^{ε}, through Eq. (53)$^{(76)}$. These different types of measurements had previously led to inconsistencies.

All these results showed that the problem of mixtures at low pressures can be systematically treated by an EOS of the VDW type and that such treatment contains as particular cases solution theories previously obtained by restricted particular models. Thus, Eq. (47) should be better than the old models. Nevertheles, the extensive application of this extended VDW theory of solutions was prevented at the time by the poor knowledge of the appropriate generalization of the VDW-EOS, and by the corresponding ignorance about the correct effective VDW parameters. The later development of the SW-EOS and its application to pure fluids, which is within the framework of the VDW model, as described in the previous sections of this article, has make it worthwhile to use Eq. (47) and a SW EOS to calculate excess functions. This work is currently under way in collaboration with Guzmán and Muñoz$^{(77)}$.

B. *SWPT for mixtures and mixing rules*

Besides the development of an EOS for mixtures, and to furnish it with a statistical basis, the SWPT was generalized to the multicomponent case in collaboration with Monfort$^{(78)}$. The generalization of the SW expansion, Eq. (25), to the multicomponent system is straightforward and leads to a definition of an effective diameter $\sigma_{\alpha\beta}$ and range $R_{\alpha\beta}$ for the interaction of species α with β. In its simplest form the SWPT for mixtures uses the BH-type α-expansion and leads to

$$\sigma_{\alpha\beta} = \int_0^{r^m_{\alpha\beta}} [1 - \exp\{-\beta(\varepsilon_{\alpha\beta} + u_{\alpha\beta})\}]\, dz \quad , \tag{60}$$

$$R_{\alpha\beta} = r^m_{\alpha\beta} - [\exp(-\beta\varepsilon_{\alpha\beta}) - 1]^{-1} \int_{r^m_{\alpha\beta}}^{\infty} [\exp(-\beta u_{\alpha\beta}) - 1]\, dz \ . \tag{61}$$

These expressions were used, together with the SW-EOS, Eq. (36), to predict the excess functions of mixing for the systems Ar + Kr and Ar + CH$^{(78)}$. The SW EOS was taken to second order and the terms a_1 and a_2 calculated from the Henderson *et al.* expressions$^{(52)}$. The theory was shown to predict correctly the excess functions g^{ε} and h^{ε} if the crossed interaction energy $\varepsilon_{\alpha\beta}$ was fitted by means of an adjustable parameter.

Essential ingredients of the VDW-OFT are the mixing rules that define the parameters of the pure fluid that represents the mixture. The joint use of the SWPT and the MCS were shown to produce essentially exact mixing rules. In order to make the pressure of the mixture equal to that of its equivalent fluid, it is sufficient to make

$$\sigma^3 g_{SW}(\sigma^+) = \sum_{\alpha,\beta} x_\alpha x_\beta \sigma^3{}_{\alpha\beta} g_{\alpha\beta}(\sigma^+{}_{\alpha\beta}) \quad , \tag{57}$$

$$R^3(e^{\beta\varepsilon} - 1) g_{SW}(R^+) = \sum_{\alpha\beta} x_\alpha x_\beta R^3{}_{\alpha\beta}(e^{\beta\varepsilon_{\alpha\beta}} - 1)\ g^{SW}_{\alpha\beta}(R^+{}_{\alpha\beta}) \tag{58}$$

and

$$\varepsilon = \sum_{\alpha\beta} x_\alpha x_\beta \varepsilon_{\alpha\beta} \quad . \tag{59}$$

These exact mixing rules require, for their practical application, to approximate the SW radial distribution functions g_{SW}. At low densities and high temperatures $g_{SW} \rightarrow 1$ and one recovers the popular VDW mixing rules

$$\sigma^3 = \sum_{\alpha,\beta} x_\alpha x_\beta \sigma^3{}_{\alpha\beta} \tag{60}$$

and

$$\varepsilon R^3 = \sum_{\alpha,\beta} x_\alpha x_\beta R^3{}_{\alpha\beta} \varepsilon_{\alpha\beta} \quad . \tag{61}$$

Thus, Eqs. (57-59) allow a systematic improvement of the VDW rules, (60) and (61), and involve a local composition effect through the rdf g_{SW}. Again, the systematic study of the SW mixing rules requires a good enough SW EOS.

VII. CONCLUSIONS AND PERSPECTIVE

The work which has been reviewed in these pages has lead to a theoretical equation of state with the following characteristics:

1) It is of the generalized VDW type, with a repulsive HS term and an attractive term of the SW form.
2) The parameters of the EOS have a physical meaning: they are related to the intermolecular potential through the (approximate) PT relations, and allow a kinetic interpretation as mean collision parameters; this interpretation has been proved rigorously at the zero density limit.
3) The EOS parameters can be calculated approximately by means of perturbation methods from the intermolecular potential, and, when the latter is unknown, by means of the phenomenological method of corresponding systems from thermodynamic data.
4) The EOS can be applied to mixtures in the context of a VDW one-fluid model. It incorporates as particular cases some well-known solution models and leads to exact mixing rules in terms of radial distribution functions defining local compositions.

In order to reach full applicability, the approach to a TEOS reviewed here requires the development of several points, some of which are currently under way: a more accurate SW EOS in closed-form expression is needed; non-spherical reference systems have to be incorporated in order to cope with more complicated molecules; the kinetic interpretation of the EOS parameters has to be extended to higher densities, and finally, the MCS has also to be extended away from the orthobaric states. All these developments are well-defined research problems whose solution would produce a physically sound and useful TEOS for real fluids.

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