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Progress in the Perturbation Approach in Fluid and Fluid-Related Theories

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I. Introduction

Since the formulation of the so-called high temperature series expansion (HTSE) by Zwanzig,[1] thermodynamic perturbation theories developed along this line have been one of the most fruitful procedures to obtain the thermodynamic properties of fluids and solids, and this is reflected in most of the books published on liquid state physics.[2] However, most of these books devote only a few pages to perturbation theories, limiting the contents to the most common topics on the subject, although some books[3−5] and review articles[6,7] include a more extensive analysis of perturbation theories, particularly the excellent review by Barker and Henderson.[6]

The perturbation strategy not only plays an important role in the calculation of bulk fluid thermodynamic properties in the context just mentioned but also, in recent years, has become more and more important in the calculation of bulk solid thermodynamic properties, in classical density functional theory, and in the Ornstein−Zernike integral equation theory. In addition, various novel perturbation methods have been formulated to tackle some chemical problems whose theoretical handling in the past depended to a great extent on macroscopic thermodynamic approaches.

In the last two decades approximately, there have been significant advances in all these kinds of theories. In spite of this, there is not available a review covering the recent advances in all these topics. In this review, not only we will include progress of the thermodynamic perturbation theory for the bulk fluid and bulk solid phases, but we also will outline the progress of the perturbation strategy in classical density functional theory, in the Ornstein−Zernike integral equation theory, and in applied research on problems of chemical interest.

Perturbation procedures proposed in each of the fields just mentioned have acquired such importance and development that they would deserve an independent review for each of the fields. The reason for grouping them together in a single review is that, as we will see later, the different fields are not unrelated; on the contrary, theories developed within one of these fields are useful in another. Therefore, an overview to the developments about perturbation theories in all these fields seems to us particularly useful. We will devote special attention to the most novel theories and applications, that will deserve more attention in the nearest future.

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Shiqi Zhou graduated in Food Engineering in 1989 at the Hunan University of Arts and Science, China, and received his Ph.D. in 1997 from the South China University of Technology under the direction of Professor Siyuan Guo. Now he is a theoretical physics professor at Central South University. Zhou's main research activity has been Statistical Mechanics Theory in the field of Liquid State Physics. He has single-authored more than sixty articles and coauthored more than thirty articles. His main teaching activity is focused on Liquid Theory. He made two major contributions to Liquid Theory: initiated using the universality principle of the free energy density functional to construct the classical density functional approximation; proposed a coupling parameter series expansion amenable under high order truncation and sped up convergence and implemented a nonhard sphere perturbation scheme in his expansion to successfully conquer the low temperature problem perplexing the Liquid Theory over a long period of time.

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II. Progress in Perturbation Theories for Bulk Fluid and Solid Phases

Some of the most recent advances in perturbation theories for simple fluids are related to the so-called λ-*expansion*. A detailed and excellent account of this expansion can be found in ref 3. We will give here only a brief summary for reference.

Let us consider a spherically symmetric pair potential $u(r)$ consisting of the sum of two contributions, a reference potential $u_0(r)$ and a perturbation $u_1(r)$. Let us now couple these two contributions by means of a parameter λ, with $0 \le \lambda \le 1$, to form a new potential $u(r,\lambda)$ of the form

$$u(r, \lambda) = u_0(r) + \lambda u_1(r) \tag{1}$$

so that, for $\lambda = 0$, $u(r,\lambda)$ reduces to the reference potential and, for $\lambda = 1$, we recover the full $u(r)$ potential of the system of interest. Then, the Helmholtz free energy can be expanded in a power series of λ in the form

$$F(\lambda) = F_0 + \left(\frac{\partial F}{\partial \lambda}\right)_{\lambda=0}\lambda + \frac{1}{2}\left(\frac{\partial^2 F}{\partial \lambda^2}\right)_{\lambda=0}\lambda^2 + ... \tag{2}$$

where F_0 is the free energy of the reference system with potential u_0.

II.1. High Temperature Series Expansion and Its Most Recent Developments

For the fluid with the full potential $u(r)$, the series 2 leads to[3]

$$\beta F = \beta F_0 + \beta\langle\Phi_1\rangle_0 - \frac{1}{2}\beta^2(\langle\Phi_1^2\rangle_0 - \langle\Phi_1\rangle_0^2) + ... \tag{3}$$

where $\beta = 1/kT$, in which k is the Bolzmann constant and T is the absolute temperature, the angular brackets mean an average, which is performed in the reference system (subscript 0), and

$$\Phi_1 = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u_1(r_{ij}) \tag{4}$$

is the contribution to the configurational energy of the system due to the perturbation $u_1(r)$.

From eq 3, the free energy of the system can be expressed as an inverse temperature expansion whose terms are related to fluctuations around the mean perturbation energy calculated in the reference system. This is the so-called *high temperature series expansion* (HTSE), first developed by Zwanzig[1] in a somewhat different way.

Expression 3 is the basis for the calculation of several of the low-order perturbative terms by means of computer simulation, as we will see later, but it is not appropriate for theoretical calculations. For the latter purpose, a more appropriate expression can be obtained by expressing the free energy of the fluid with pair potential 1, with $\lambda = 1$, in the alternative way[3]

$$\frac{F}{NkT} = \frac{F_0}{NkT} + \frac{2\pi\rho}{kT}\int_0^1 \mathrm{d}\lambda \int u_1(r)\, g(r, \lambda) r^2\, \mathrm{d}r \tag{5}$$

and taking for the radial distribution function (rdf) $g(r,\lambda)$ of the fluid with pair potential 1 its series expansion in terms of λ

$$g(r, \lambda) = g_0(r) + \left.\frac{\partial g(r, \lambda)}{\partial \lambda}\right|_{\lambda=0}\lambda + ... \tag{6}$$

where $g_0(r)$ is the rdf of the reference fluid. This allows us to obtain the derivatives involved in expansion 2. The first derivative

$$\left.\frac{\partial(F/NkT)}{\partial\lambda}\right|_{\lambda=0} = \frac{2\pi\rho}{kT}\int u_1(r)\, g_0(r) r^2\, \mathrm{d}r \qquad (7)$$

involves only the rdf of the reference fluid, which often is available from integral equation theories. Expression 7 was also derived by Zwanzig[1] in a somewhat different way.

The higher order derivatives involve higher order correlation functions of the reference fluid, which cannot be easily obtained, so that theoretical calculations of higher order terms can be carried out only in an approximate way.

In any case, the above-mentioned procedures lead to express the thermodynamic and structural properties as series expansions in the inverse of the reduced temperature $T^* = kT/\varepsilon$. Thus, for example, the Helmholtz free energy

$$\frac{F}{NkT} = \sum_{n=0}^{\infty}\frac{F_n}{NkT}\frac{1}{\mathrm{T}^{*n}} \qquad (8)$$

and the rdf

$$g(r) = \sum_{n=0}^{\infty} g_n(r)\frac{1}{\mathrm{T}^{*n}} \qquad (9)$$

Monte Carlo Perturbation Theory

Henderson et al.[8,9] developed a procedure to obtain the first few terms in the perturbative expansions from simulations performed in the reference system on the basis of eq 3. The zero- and first-order terms in expansion 9 are given by[9]

$$g_0(r_i + \Delta r/2) = \frac{3\langle N_i\rangle_0}{2\pi N\rho(r_{i+1}^3 - r_i^3)} \qquad (10)$$

and

$$g_1(r_i + \Delta r/2) = -\frac{3\sum_j \{\langle N_i N_j\rangle_0 - \langle N_i\rangle_0\langle N_j\rangle_0\} u_1^*(r_j)}{2\pi N\rho(r_{i+1}^3 - r_i^3)} \qquad (11)$$

respectively, where N_i is the number of intermolecular distances in the range (r_i, r_{i+1}), with $\Delta r = r_{i+1} - r_i$, $i = 0, 1, ...$, and $u_1^*(r) = u_1(r)/\varepsilon$.

From the corresponding terms of the rdf, the zero- and first-order terms in the expansion of the compressibility factor and the first- and second-order terms in the expansion of the excess internal energy can easily be obtained using the virial and energy equations, respectively. The corresponding terms for other thermodynamic properties can be obtained from standard thermodynamic relationships.

Several authors have performed this kind of simulations for the square-well (SW)[8-13] and, very recently, for other potential models with a hard spherical core such as the Sutherland[14,15] and the triangular-well (TW)[16] potentials. These simulations show that the second-order term in the free energy expansion is approximately 1 order of magnitude smaller than the first-order term, and the third-order term is[10] 1 order of magnitude smaller than the second-order term, so that often can be neglected. Moreover, the statistical uncertainty of the third-order term is of the same order of magnitude as the term itself. Within the framework of the HTSE, these simulations can be considered as "exact", as no theoretical approximation is involved. Therefore, they signal the limiting accuracy achievable for any theoretical approximation. The comparison of the results obtained from the perturbative expansion truncated at first order in the rdf and the compressibility factor and at second order in the free energy, with the perturbative terms obtained in the way just described, with the actual simulation data for the square-well fluids reveals an overall excellent accuracy for supercritical temperatures. The agreement worsens as temperature, potential range, and density decrease.

Alder et al.[10] reported parametrizations for the perturbative terms F_n/NkT, with $1 \le n \le 4$, of the free energy of the SW fluid with well width $\lambda = 1.5$ derived from computer simulations. Barker and Henderson[17] also reported parametrizations for the same value of λ for F_n/NkT, with $n = 1, 2$, obtained on the basis of their computer simulation data for the same quantities.

The MC procedure for obtaining the first- and second-order terms in the perturbative expansion (eq 8), just described, was applied also to the Lennard-Jones (LJ) fluid,[18] although the MC data for F_1 and F_2 were reported only in graphical form. Very recently, new MC data for F_1 and F_2 have been reported for this potential model.[19]

In a recent paper,[20] the MC procedure has been used to obtain the first three terms in the perturbative expansion of the free energy for liquid cooper, using a soft-sphere reference system. The results obtained show that the series truncated at second order provides virtually exact results when optimal parameters are used for the reference potential.

Barker–Henderson Second-Order Perturbation Theory

In the Barker–Henderson theory,[21] the first-order term in expansion 8 is the same as in the expression resulting from eq 7, namely

$$\frac{F_1}{NkT} = 2\pi\rho\int_0^{\infty} u_1^*(r)\, g_0(r) r^2\, \mathrm{d}r \qquad (12)$$

For the second-order term, they propose two approximations, namely the *macroscopic compressibility approximation* (MCA)

$$\frac{F_2}{NkT} = -\pi\rho kT\int_0^{\infty}[u_1^*(r)]^2\left(\frac{\partial\rho}{\partial p}\right)_0 g_0(r) r^2\, \mathrm{d}r \qquad (13)$$

and the *local compressibility approximation* (LCA)

$$\frac{F_2}{NT} = -\pi\rho kT\int_0^{\infty}[u_1^*(r)]^2\left(\frac{\partial[\rho g_0(r)]}{\partial p}\right)_0 r^2\, \mathrm{d}r \qquad (14)$$

The values of F_1/NkT calculated from eq 12 are in excellent agreement with those calculated from simulation, provided that we use an accurate expression for $g_0(r)$. Instead, the second-order term F_2/NkT calculated either from eq 13 or from eq 14 strongly underestimates the magnitude of the corresponding simulation values for the SW fluid at high densities for any well-width λ and even at low densities for small well widths.[11] A procedure to sum up the series within the macroscopic compressibility approximation has been derived,[22,23] but the contribution of the higher-order terms within this approximation is very small.[22]

Smith et al.[18] derived a more accurate expression for the second-order term in the free energy expansion. This approximation was shown[11] to provide much better agreement with the simulation data of F_2/NkT for the SW fluid than the LCA or MCA approximations. The agreement was very satisfactory for low to moderate densities for potential widths $1.1 \leq \lambda \leq 2.0$ and semiquantitatively correct at higher densities for $1.6 \leq \lambda \leq 2.0$. The procedure has the drawback that it requires quite complex numerical calculations. An analytical expression for this term based on similar grounds was reported in ref 24.

Simple analytical expressions for the first- and second-order terms in HTSE of the free energy of the square-well fluid of variable width have been developed by several authors.[25−28] Using similar procedures, such as those derived in refs 24−26, the first-order perturbation theory has been recently applied to the TW fluid.[29]

The inverse temperature expansion of the free energy of the SW fluid can be used for the square-shoulder (SS) fluid too and can be generalized to any number of potential wells, or shoulders, or combinations of the two. This is the basis of a discretization procedure[30] that allows one to obtain the thermodynamic properties of fluids with continuous potentials on the basis of the perturbation theory for the SW fluid or parametrizations based on it.

The Barker−Henderson theory can be applied as well to potentials with a soft core. This can be achieved by defining a suitable temperature-dependent effective diameter,[31] although the definition of the effective diameter is not unique and the accuracy may be affected by the definition adopted.[32] The BH theory in the MCA approximation has been improved recently in two ways.[33] In the first place, an empirical correction was introduced into the MCA for F_2. In the second place, a new definition of the effective diameter for soft-core potentials, leading to an exact prediction of the second virial coefficient, was adopted. Moreover, by using an approximate expression for the rdf of the HS reference fluid and for the various integrals involved, the theory was formulated in an analytical way for several model potentials. The BH theory modified in these ways leads to improved prediction of the liquid−vapor coexistence as well as accurate prediction of the thermodynamic properties of these model fluids.

The Weeks−Chandler−Andersen Perturbation Theory

A more appropriate choice of the effective diameter leads to the Weeks−Chandler−Andersen (WCA) perturbation theory,[34] in which the second-order term in the free energy expansion is negligible. While the BH effective diameter is only temperature dependent, the WCA effective diameter is temperature and density dependent. Simple parametrizations for the BH and WCA effective diameters for the Lennard-Jones fluid have been reported by Verlet and Weis.[35] For this potential model, the results of the WCA theory are superior to those of the BH theory either in the MCA or in the LCA approximations. The reliability of several equations of state for the hard-sphere fluid and the effect of different choices of the effective diameter for reproducing the thermodynamic properties of the WCA reference system have been analyzed in ref 36. However, for potentials softer than the LJ potential, Lado has shown[37] that the WCA predictions can be improved by combining the WCA prescription for the rdf of the reference system with a thermodynamic self-consistency condition.

The WCA theory is not suitable for densities close to the freezing line, because the effective hard-sphere diameter becomes so large that the reduced density of the reference hard-sphere fluid lies in the metastable fluid region,[38] for which it is difficult to obtain good theoretical solutions for the rdf $g_0(r)$ of the hard-sphere fluid. It has been proposed either to use a reduced effective diameter at high densities by introducing a density-dependent cutoff distance for the reference potential,[38] instead of a fixed cutoff distance at the minimum of the potential as in the original WCA theory, or to use a reference potential whose repulsive range decreases as density increases.[39] These two procedures lead to improved accuracy of the WCA theory in the high density region for a number of simple potential models.

The WCA theory was modified by Ben-Amotz and Stell[40] by using directly a hard-sphere reference system, instead of indirectly using a soft-repulsive reference system which in turn is related to the HS system. The modified WCA theory is more flexible with the choice of the effective HS diameter while providing nearly the same results as the original WCA for LJ fluids.

Very recently, Heyes and Okumura performed molecular dynamics (MD) simulations for the equation of state of the WCA reference fluid and fitted the results to a simple equation of state.[41]

Simple Crystalline Solids

The Monte Carlo (MC) procedure for obtaining the first few terms in the inverse temperature expansion of the thermodynamic and structural properties can also be applied to crystalline solids.[15] The same is true for first-order perturbation theory,[42,43] the Barker−Henderson second-order perturbation theory,[15,44−46] and the WCA perturbation theory.[47−50] On the basis of the WCA theory, a simple parametrization of the free energy for LJ solids has been developed[51] which provides excellent agreement with experimental data for the melting curves of simple solids. Solid−solid transitions in systems with hard-sphere potential with added short-ranged soft repulsions beyond the hard core were studied by means of first-order perturbation theory.[52] It was found that the presence of the soft repulsion leads to a rich variety of crystalline structures.

Several recent papers[53−55] analyzed the reliability of the first-order perturbation theory, with either the BH or the WCA choices for the effective diameter of the HS reference system, to predict the thermodynamic properties of simple fluids and solids. It was found that the first-order WCA theory accurately predicts the solid−liquid equilibria in LJ models of simple systems[53] as well as for other potential models with a hard spherical core[54] of the type used in models of colloidal suspensions. In the latter kind of potential models, the first-order theory also provides reasonable results for the fluid−fluid transition for not too short-ranged potentials, whereas for very short-ranged potentials the theory gives unphysical results.[54]

The accuracy of the first-order perturbation theory for obtaining the thermodynamic properties of fluids with repulsive interactions with diverse degrees of softness and attractive interactions with diverse ranges was analyzed in ref 55. It was found that for purely repulsive potentials the WCA theory only fails for potentials much softer than the repulsive part of the Lennard-Jones potential. Concerning the attractive interactions, the theory was shown to be very accurate for the LJ potential except perhaps near the critical density and at very low densities. In both cases, the first-order BH theory gave slightly poorer results. The region of inaccuracy in the WCA theory widens as the range of the attractive interactions decreases, but the theory is still accurate in the high density region. This suggested[55] the usefulness of the WCA theory to study several interesting properties arising in some fluids at high densities, such as the anomalous behavior of certain thermodynamic properties or the disappearance of the critical point as the attractive interactions become more and more short-ranged.

Perturbation Theory for Systems with Strongly Repulsive Interactions

Zwanzig's HTSE[1] is expected to fail when the perturbation $u_1(r)$ is strongly repulsive and rapidly varying or singular. To cope with such situations, it was proposed[56] to use a new imaginary potential $u(r,\lambda)$, instead of the usual eq 1, in the form $u(r,\lambda) = u_0(r) - \ln(1 + f\lambda(r))$, where $f(r) = \exp(-u\beta_1(r)) - 1$ is the Mayer *f*-function for the perturbation $u_1(r)$ of the actual potential. Then, following the standard procedure,[1,5] a new perturbation series can be derived. The series truncated at first order was applied[56] to a one- and three-dimensional model potential consisting of the hard core plus a shoulder of constant positive magnitude, plus a weak long-range attraction term, and an extension to mixtures was also derived. Recently, the second-order term in the expansion has been derived[57] with the help of the BH local compressibility approximation.[21] It was shown[57] that the second-order theory provides satisfactory agreement with the existing simulation data for a hard-sphere fluid in which the diameters of the spheres are increased from σ to $\sigma(1 + \Delta)$ as well as for binary mixtures' nonadditive hard spheres with shoulders. Higher order terms of the series become progressively more and more complicated, and no reasonable approximations are available; an exception is an effective two-component system[58] onto which a mixture consisting of hard-sphere colloids, with radius R_c, and self-avoiding polymer coils, with radius of gyration R_g, can be mapped; for this effective two-component system, the third-order term is tractable.

II.2. Variational Perturbation Theory

Another approach to obtain the thermodynamic properties of simple fluids is the *variational perturbation theory* proposed by Mansoori and Canfield.[59,60] It is a first-order perturbation theory based on the Gibbs−Bogoliubov inequality

$$F \le F_0 + \langle \Phi_1 \rangle_0 = F_0 + 2\pi N\rho \int u_1(r)\, g_0(r) r^2\, \mathrm{d}r \tag{15}$$

Taking for the reference system a fluid of hard spheres with diameter σ, the right-hand side of the precedent equation can be expressed in terms of the reduced quantities $r^* = r/\sigma$ and $\rho^* = \sigma\rho^3$. Then, minimizing the right-hand side of eq 15 with respect to σ will render the inequality close to equality.

The variational procedure has been applied with success to the Lennard-Jones potential and is frequently used to obtain the thermodynamic properties of liquid metals. However, it has been argued[61−64] that the use of the hard-sphere reference potential for fluids with soft-core potentials may be inappropriate in perturbation theories. This is due to the fact that a region of the phase space, available to the actual system, is discarded in the perturbation theory because of the impenetrability of the hard spheres. In some cases, this drawback can be removed by using a soft-sphere reference system.[65,66] Another possibility is to introduce a correction into the perturbation theory based on the hard-sphere reference system. It has been shown[62−64] that by calculating by means of Monte Carlo simulation the correction within the context of the variational theory, accurate upper and lower bounds that closely bracket the free energy of the actual system can be obtained. Very recently, an analytical expression for the correction in terms of the rdf of the Lado's self-consistent WCA theory[37] has been developed.[67] The variational perturbation theory with this analytical correction provides better accuracy than the WCA, self-consistent WCA, and variational perturbation theory, for soft-sphere fluids[67] and liquid metals.[68]

Very recently, a *variational associating fluid theory*, derived on the basis of the variational perturbation theory with a soft-sphere reference system, has been proposed to obtain the equation of state of expanded liquid mercury.[69] The theory predicts very accurately the gas−liquid coexistence curve for that system.

II.3. Optimized Cluster Theory

Another diagrammatic expansion, denoted *optimized cluster theory* (OCT), was developed by Andersen et al.[70,71] As particular cases, the OCT leads to the *random phase approximation* (RPA), the *optimized random phase approximation* (ORPA), and the *exponential approximation* (EXP), among other approximations. In all these approximations, the free energy of the fluid is expressed in terms of the rdf of the reference fluid. The RPA, ORPA, and EXP approximations can also be considered from the viewpoint of integral equation theories in which the Ornstein−Zernike equation is solved using closure conditions that involve the correlation functions of the reference fluid. Again, these approximations were analyzed with detail in refs 3−6, and so we will not extend too much in their discussion.

The ORPA and other related approximations are widely used to obtain the structure factors of simple liquid metals. Conversely, they can be used to obtain effective interaction potentials from measured structural data.

Regnaut[72] compared the results obtained from the variational and ORPA theories for the thermodynamic properties of liquid metals, using a hard-sphere reference system. He concluded that the second of these theories is more suitable to account for the influence on the energy of the softness and the long-range oscillations of the potential and, therefore, it is more accurate for analyzing the thermodynamic stability. This is related to the fact that, contrarily to the ORPA, the variational theory with the HS reference system does not account for the deviation of the structure of the metal with respect to that of the HS system. However, it is to be noted that, as mentioned previously, the variational theory can be used with reference systems other than the HS fluid. In contrast, the ORPA in its original formulation cannot be directly used with non-HS reference potentials. A general formulation of the ORPA with continuous reference potentials was developed by Pastore et al.[73] The procedure was subsequently applied[74] to successfully obtain the thermodynamic and structural properties of several liquid metals with an accuracy superior to that provided by the variational theory.

In its original form, the ORPA approximation is not well suited for very short-ranged interactions. Quite recently, a modification, denoted *nonlinear ORPA*, has been proposed,[75] giving rise to a significant improvement for these kinds of interactions.

The applications of the ORPA and related theories reported in the past decade include the study of the phase diagrams of fluids in disordered porous materials[76] and the thermodynamic properties of colloidal suspensions.[46,77]

II.4. Wertheim Thermodynamic Perturbation Theory for Association

An important development in the study of associating fluids has been the TPT due to Wertheim,[78−81] who derived his theory by expanding the Helmholtz energy in a series of integrals of molecular distribution functions and the association potential. Then, the resulting complex expression is simplified by using physical arguments, which are based on steric incompatibility due to the potential model used, to remove many of the integrals in the series. The conventional starting point for simple and multipolar fluids is an expansion in the singlet density, which however leads to cumbersome and inefficient graph cancellation. Wertheim employed an expansion in the fugacity, z, and developed a formulation of statistical thermodynamics in terms of two density variables, the usual singlet density, and the monomer density. The two-density formalism is of strong structural similarity to the usual formulation of the statistical thermodynamics of simple and multipolar fluids, which is based on singlet density alone and optimizes the exploitation of steric incompatibility effects. One attractive feature of Wertheim's TPT is that the final general result is of surprising simplicity. Wertheim applied the first-order version of his TPT (TPT1) to the thermodynamics of hard dimers and longer hard chain molecules.[82,83]

Ghonasgi and Chapman[84] and independently Chang and Sandler[85] developed a dimer version of the TPT (TPTD) using a concept similar to that of Wertheim's TPT1 but with the reference system represented by a fluid of dimers. The TPTD was employed to investigate the structural and thermodynamic properties of a monodisperse Yukawa hard-sphere chain fluid, and it was found[86] that overall the TPTD gives more accurate predictions than the SAFT-VR (see below). Recently, the TPTD was extended[87] to treat a polydisperse mixture of the Yukawa hard-sphere chain fluid with chain length polydispersity, obtaining successfully the full liquid−vapor phase diagram, including critical binodal, cloud, and shadow curves and distribution functions of the coexistence phases, in qualitative agreement with the corresponding experimental predictions for the polydisperse mixture of polymers in a single solvent.

Gubbins and co-workers[88−90] generalized Wertheim's work in a simple, unified formalism, to study problems ranging from the chemical equilibrium of simple fluids to the equation of state of mixtures of heteronuclear chains. The resulting approach is termed *statistical associating fluid theory* (SAFT), which has proven to be a powerful approach for modeling associating and nonassociating chain fluids and their mixtures.

In the SAFT framework, different microscopic contributions that control the macroscopic properties of the fluids are explicitly considered. The free energy in the original SAFT is hence written as a sum of four separate contributions as follows:

$$\frac{A}{NkT} = \frac{A^{\mathrm{ideal}}}{NkT} + \frac{A^{\mathrm{mono}}}{NkT} + \frac{A^{\mathrm{chain}}}{NkT} + \frac{A^{\mathrm{assoc}}}{NkT} \qquad (16)$$

where N is the number of molecules, A^{ideal} is the ideal free energy, A^{mono} is the contribution to the free energy due to the monomer segments, A^{chain} is the contribution due to the formation of bonds between monomer segments, and A^{assoc} is the contribution due to association. Different versions of the SAFT equation mainly differ in the monomer term, as will be explained later on. The possibility of extending Wertheim's TPT1 to treat solid phases has only recently been explored and employed to study the liquid−solid phase equilibrium of chain molecules.[91−93]

The SAFT is perhaps the most versatile engineering equation of state in use today. The great success of the SAFT-type equations is due to their accuracy and applicability to systems and properties for which other equations fail. Clearly it is the strong statistical mechanical basis of these equations that justifies their success. The extension to mixtures, polar fluids, molecular liquids, electrolyte solutions, and inhomogeneous fluids leads to more sophisticated versions of the theory, that will be discussed in this and other sections. Besides the original SAFT (SAFT-HS) version, describing molecules as chains of hard-sphere segments with long-range dispersion forces treated at the van der Waals mean field level, and the engineering version HR-SAFT,[94−96] which extends the original SAFT to many real, molecular, and macromolecular fluids and their mixtures and represents a useful, predictive correlation for these fluids, we also have other versions, such as the so-called soft-SAFT[97−100] and the SAFT-VR.[28,101] In the soft-SAFT the monomer term is a spherical LJ fluid which accounts for both the repulsive and attractive interactions of the monomers forming the chain. The SAFT-VR describes chain molecules formed by hard-core monomers with attractive potentials of variable range and significantly improves upon the van der Waals mean field treatment used in the SAFT-HS approach by providing an additional parameter characterizing the range of the attractive part of the potential. Further modifications and developments of the SAFT-VR have been developed fruitfully and lead to, to name but a few, the group-contribution SAFT,[102] termed as SAFT-γ, the SAFT-VRE,[103] dealing with strong-electrolyte solutions, the SAFT1-RPM[104,105] and SAFT2-RPM,[106,107] for general electrolyte solutions, and the SAFT-VR+D,[108−110] for dipolar fluids and dipolar associating fluids.

The SAFT-VRE models the water molecules as hard spheres with four attractive short-range sites to describe the hydrogen-bonding association, the salt molecules are modeled with two hard spheres of different size which describe the anion and cation, respectively, the ion−ion interactions are included at the simplest restricted primitive level in the form provided by the mean spherical approximation, while the long-range water−water and ion−water attractive interactions are modeled as square-well dispersion interactions in the spirit of the SAFT-VR.[28,101] Due to the incorporation of an explicit description of the solvent, the experimental vapor pressures and densities are very well described by the SAFT-VRE approach by using only one transferable fitted parameter per ion. The SAFT1-RPM couples the SAFT-VR[28,101] with the restricted primitive model and can represent both single-salt and multiple-salt solutions, including their activity coefficients, osmotic coefficients, vapor pressures, and densities. In the SAFT1-RPM approach, each salt consists of two distinct segments, the cation and the anion, and is characterized by one parameter, namely the salt hydrated diameter, and each ion is characterized by three parameters, namely the ion volume, energy, and square-well width. However, the application of the SAFT1-RPM approach is limited to monovalent ions due to a limited range of the square-well width parameter needed to estimate the effective reduced density for use in the calculation of the monomer term. By relaxing the range of the square-well width parameter, the SAFT1-RPM can be extended to multivalent ions: single salt + water solutions and multiple-salt solutions including seawater/brine. The resulting SAFT2-RPM, which differs from the SAFT1-RPM by a new dispersion-term approximation and a new set of salt and ion parameters values, has the same parameters as those used in the SAFT1-RPM. The SAFT-VR+D explicitly accounts for the position and orientation of the dipole moment and incorporates its effect on the structure of the fluid through the use of a dipolar square-well reference fluid treated by a generalized mean spherical approximation (GMSA). It has been shown that the phase behavior and thermodynamic properties of a dipolar square well monomer, chain fluids, in which one or more segments are dipolar, and dipolar associating square-well monomers with one, two, and four association sites may be described satisfactorily by the SAFT-VR+D.

The SAFT-γ[102] is a heteronuclear generalization of the SAFT-VR and can tackle heteronuclear molecules which are formed from fused segments of different types. The parameters of various functional groups, namely the group size, dispersive energy and range, and shape factor, together with the unlike energy parameters between different groups, are adjusted to give an optimal description of the vapor−liquid equilibrium for an extensive selection of pure compounds comprising the CH_3, CH_2, CH_3CH, ACH, $ACCH_2$, $CH_2=$, $CH=$, and $-OH$ groups. The main advantage is that the binary interaction parameters between groups can be obtained directly from the pure components alone. The predictive capability of the SAFT-γ is demonstrated by calculating the vapor liquid equilibrium of some larger compounds comprising those groups which are not included in the optimization database.

Although the traditional simple cubic EOSs[111] represent the thermodynamic properties of pure fluids and fluid mixtures accurately, these equations do not consider the real size and shape differences between the pure components and are not thermodynamically self-consistent. As a result, the predictive capabilities of these equations are limited. The success of the SAFT in complex fluids may lie in the applicability of its different extensions and variants to the calculation of bulk *PVT* and phase behavior properties[112−115] and interfacial properties,[116−118] of a wide range of industrially important systems, such as, for example, simple alkanes,[28,119,120] simple polymers and their mixtures,[113,121−123] perfluoroalkanes,[124,125] hydrogen fluoride,[126] boron triflouride,[127] water,[128,129] refrigerant systems,[130] carbon dioxide,[131,132] electrolyte solutions,[103−107,133−135] surfactant systems,[136] etc.

It should be pointed out that the Wertheim's theory also provides a promising framework for treating the thermodynamics of a wide range of self-assembling systems.[137] On the other hand, a TPT for association with bond cooperativity was derived from a more intuitive but less rigorous method.[138] It has been claimed[138] that the method is very generally applicable and can be used to rederive Wertheim's perturbation theory for dimerization[78,79] and for chain formation.[80,81]

It is to be noted that Wertheim's theory also comprises the multidensity Ornstein−Zernike integral equation, which has played an important role in the investigation of homogeneous and inhomogeneous chemically associating fluids.[139,140] However, we will not give further discussion because the field is out of the domain of the perturbation approach.

A general problem of the TPT for atomic fluids, i.e. overprediction of the critical temperatures of pure components, is also not exceptional to the TPT1 and the abovementioned related theories. In chain molecule solutions, this undesirable character even becomes more acute when the critical temperature is measured relative to that of the more volatile component; and what is more, the magnitude of the problem is even not weakened simply by adjusting the parameters of the pure component, perhaps because the adjusting induces the mixture to be far more asymmetrical than it actually is. A better choice to go beyond the classical approximation is to incorporate the renormalization group treatment into the TPT framework. Such an endeavor has been performed in atomic fluid TPT and the SAFT formalism (see below).

II.5. Renormalization Group Perturbation Theory

Similarly to all empirical equations of state (EOS), all the EOSs derived from various perturbation expansions are also essentially mean field equations that fail to reproduce the nonanalytical singular behavior of fluids in the critical region caused by long-scale fluctuations in density. During the last two decades, many efforts have been made to develop a global EOS able to reproduce the classical van der Waals-like limit far away from the critical point, reducing to the ideal-gas limit at low densities, and transform it into a nonanalytical scaled EOS as the critical point is approached. The theoretical models most influential are probably the hierarchical reference theory (HRT) developed by Parola and co-workers,[141] the global renormalization group (RG) procedure proposed by White and co-workers,[142] the crossover approach to global critical phenomena advanced by Chen at al.,[143,144] and a phenomenological approach by Kiselev et al.[145] As the HRT principally falls into the field of the distribution function formalism, we will not refer to it in the analysis that follows.

Crossover Approach to Global Critical Phenomena

As the validity of the asymptotic power law is restricted to a very small region near the critical point, and the classical EOSs completely fail close to the critical point, the crossover approach dealing with nonasymptotic behavior of fluids, including the crossover from Ising behavior in the immediate vicinity of the critical point to classical behavior far away from the critical point, is essential for formulating an EOS accurately describing the behavior of fluids over the entire thermodynamic surface. Such an approach has been developed by Chen at al.,[143,144] Jin et al.,[146] and Kiselev et al.[145,147] by following the work of Nicoll et al.[148] The crossover approach is based on the Landau−Ginzburg−Wilson theory of critical fluctuations and leads to a renormalized classical Landau expansion to take into account the effects of the long-scale fluctuation in density. It has been pointed out[143] that the crossover procedure based on a two-term Landau expansion is only adequate to obtain an asymptotic crossover model, i.e. the crossover from asymptotic singular critical behavior to asymptotic classical critical behavior. To reproduce the actual classical thermodynamic behavior observed in fluids, one needs to consider a more complete classical Landau expansion with more expansion terms. Reference 144 extended the CAS procedure so that it can be used in conjunction with a six-term classical Landau expansion, and the resulting nonasymptotic crossover renormalized free energy model was shown to compare favorably with experimental thermodynamic-property data for carbon dioxide, steam, and ethane. Other solutions to the asymptotic crossover model were also obtained by Belyakov and Kiselev[149] on the basis of an expansion in terms of $\varepsilon = 4 - d$, where d is the dimensionality, and by Bagnuls and Bervillier[150] from a 3-dimensional field theory. In ref 151 mathematical details are reported for several particular theoretical crossover models, which correspond to different approximations for the renormalization functions occurring in a differential equation for the Helmholtz free energy density resulting from the RG theory of critical phenomena.

Although these crossover equations of state give a very accurate representation of the thermodynamic properties of fluids and fluid mixtures in a wide region around the critical point, in the ideal-gas limit they do not satisfy the ideal gas equation of state and, therefore, they cannot be extrapolated to low densities. This undesirable drawback has been overcome in a global crossover EOS[152] which incorporates the classical van der Waals behavior (including the ideal-gas limit and the high density hard sphere limit) far away from the critical point and singular behavior near the critical point. This equation was obtained from a transformation derived from the renormalization-group theory of critical fluctuations to a closed-form classical EOS. As shown by Kiselev and co-workers,[152,153] the use of an universal crossover function in this global crossover procedure not only yields a better description of the *PVT* and VLE properties of pure fluids and binary mixtures in the critical region but also improves the representation of the thermodynamic surface of dense fluids in general.

Kiselev's global crossover procedure[152] has been applied to simpler versions of the SAFT EOS, giving rise to crossover SAFT EOSs in which the expressions of HR-SAFT have been used. The comparison of these equations with experimental PVT and VLE data for normal alkanes,[154] polar, and associating fluids[155] shows a noticeable improvement over the original SAFT. Kiselev's crossover procedure has also been used in combination with the more sophisticated SAFT-VR. The resulting crossover EOS, the SAFT-VRX,[156] was shown to be very accurate in the prediction of PVT and phase behavior for both nonassociating and associating fluids and mixtures.

Global Renormalization Group Procedure

White proposed a numerical procedure[142] which facilitates the development of a general renormalization group theory for real fluids capable of predicting their thermodynamic properties globally, including both at the critical point and away from the critical point, from the specification solely of the microscopic interactions between the constituent molecules. The global RG procedure[142,157] starts from any mean field expression for the Helmholtz free energy density and transforms it to the final one by including contributions from the attractive tail that correspond to density fluctuations of increasingly longer wavelengths. These contributions are evaluated approximately by using the phase space cell approximation of Wilson.[158] Unlike the RG procedure applied to the Ising and lattice gas models, the molecules in the fluid are considered capable of moving freely within the fluid rather than being restricted to particular lattice sites. In this context, the phase space cell approximation consists in treating fluctuations between two RG steps as wave packets, each of them nonvanishing and varying in amplitude, in a limited subvolume within which the fluctuations of longer wavelengths have approximately constant amplitude. Massive sample calculations[159] indicate that, after the first few iterations of the RG step, the contributions resulting from successively longer wavelength fluctuations decrease rapidly in size so that, in most cases, negligible contributions result after six iterations. The phase space cell approximation includes several parameters[142,157−159] whose values the global RG procedure, at its present stage of development, cannot determine a priori. As a result, the use of the global RG procedure to make predictions requires the specification of at least a little more than the intermolecular potential, e.g., specification of the critical point temperature, density, and pressure. It has been attempted[160] to use the global RG procedure to find the critical point parameters of the SW fluid by using simulation results for the coexisting gas and liquid densities not too close to the critical point; however, the values obtained differed substantially from estimates made previously from Monte Carlo simulations performed over similar ranges of density and temperature in combination with extrapolation methods. The theoretical formalism due to White and co-workers has been further developed. Thus, it has been extended to a larger region around the critical point,[161] to fluid mixtures,[162] to improve cubic EOSs near the critical point,[163] and to chain fluids.[164] Recently, the global RG procedure has been applied[165] to investigate multiple critical points for an isotropic pair potential with a repulsive soft core situated between the hard sphere repulsion and an attractive tail, but the theoretical results have not been compared to computer simulation results.

Merging the renormalization group concept with the liquid state theories is presently the only way to make the latter go beyond the mean field approximation. The works discussed above are undoubtedly leadings in this regard; further combination of the renormalization group with other kinds of the perturbation approach will be the focus of future research. In addition, the existence of several unknown parameters makes the renormalization group perturbation approach depart somewhat from the first principles character.

II.6. Ginzburg−Landau Theory

Ginzburg and Landau proposed[166] in the 1930s a phenomenological mean-field approach to phase transitions. Its crucial hypothesis is that in the vicinity of the critical point the free energy functional can be written in powers of the order parameter of the problem. Although the GL theory was initially conceived as a phenomenological description, a conceptual connection between the GL expansion coefficients and microscopic interaction parameters has been established.

Quite recently, there have been formulated[167] the basic principles of a generalized lattice model of multicomponent condensed systems, and a Helmholtz free energy expression that leads to a functional in a form similar to the "purely phenomenological" GL functional has been derived, with the advantage that all the parameters in the former have a simple physical interpretation and are well-defined, and the functional is not restricted on the finite number of power terms. Considering that the GL functional has been extensively used to model phase transitions in superconductors, alloys, superfluids, and crystalline solids, as well as in dynamic models of the nucleation and growth of metastable phases, and in spinodal decomposition and ordering from an initially unstable phase,[168] it would be of value to determine self-consistently the parameters characterizing this functional in terms of the microscopic variables of the underlying interaction potential.

It has been shown[169] that the parameters can be extracted with the help of Monte Carlo simulation from a multivariate distribution of energies and particle densities; the dependence of these parameters on temperature and chemical potential can be obtained by reweighing multivariate histograms compiled in a single thermodynamic state. In this way, a link is established between the atomistic and mesoscopic length scales.

Last but not least, the GL functional expression also can be derived[170] using classical DFT as a gradient expansion in terms of a set of order parameters; this results in a true long-wavelength approximation in which microscopic details are subsumed into the various coefficients of the gradient expansion. These coefficients can be calculated from microscopic information, such as moments of the *n*-body direct correlation function. An important limitation of this functional is concerned with the divergence of higher order moments in the case of interactions that decay algebraically. A theoretical way to develop the GL functional for such long-range potentials is to follow the procedure used in TPT by separating the potential into a short-range part and a long-range part and tackling the latter by the mean field approximation. Another limitation is that the free energy functional is unstable with respect to very sharp interfaces; such rapid variations in the order parameters overstep the scope of the GL approach. This functional has been used to discuss surface melting, the nucleation of freezing in a bulk fluid,[171] solid−solid phase transitions,[172] the liquid−fcc solid planar interface, the properties of small solid clusters nucleating within a liquid,[173] and the morphology of spinodal decompositions in mixtures of a liquid crystal and a colloidal particle.[174] The GL theory is also ready for investigation of the weak anisotropy of the interfacial free energy γ for the crystal−melt interface;[175] in such a GL scheme, the order parameters are the amplitudes of density waves corresponding to the principal reciprocal lattice vectors. It has been shown that the GL theory yields predictions of γ and its anisotropy in reasonably good agreement with MD simulations for Fe. Dynamics of highly viscous liquids has been investigated by a time-dependent GL equation[176] of the nonconserved type taking account of the molecular orientational fields, the stress tensor fields, and the potential energy density fields; it has been argued that the simple model is consistent with several available experimental facts. For progress on the numerical aspect of the nonconserved order parameter GL equation, the readers are referred to ref 177 and references therein.

The biggest merit of the GL approach is perhaps its serviceability in actual complex systems; this will be expatiated upon in the next sections. It should be pointed out that the extensive applicability of the GL approach, particularly to complex systems, comes from its phenomenological character. As a result, the GL approach is essentially not a first principles theory. The more microscopic intermolecular information is implanted into the mesoscopic description, the more quality going along with the first principles description will be imparted to the LG approach, but there should be a compromise between the complexity of the first principles in calculation and the universality of phenomenological description in application.

II.7. Numerical Ornstein−Zernike Integral Equation Thermodynamic Perturbation Theory

Recently, one of the present authors advanced[178] a new version of TPT which is based on a coupling parameter expansion (CPE) like that in eq 2, that can be rewritten in the form

$$\beta f = \beta f_0 + \sum_{n=1}^{\infty} \beta f_n \tag{17}$$

with

$$f_n = \frac{2\pi\rho}{n!} \int u_1(r) \frac{\partial^{n-1} g(r,\lambda)}{\partial \lambda^{n-1}}\bigg|_{\lambda=0} r^2\, \mathrm{d}r \tag{18}$$

where f is the free energy per particle, f_0 is the free energy per particle in the reference system with potential u_0, f_n is the perturbative contribution of order n to f, and $g(r,\lambda)$ is the radial distribution function of an imaginary fluid with a pair potential of the form in eq 1.

Unlike the above-mentioned high temperature series expansion, the *n*-th term in Zhou's expansion depends only on the $(n - 1)$-th derivative of the rdf $g(r,\lambda)$ of the fluid with potential (eq 1) evaluated at $\lambda = 0$. Hence, Zhou was able to formulate the third-order[178,179] and fifth-order versions[180] of the expansion in eq 17 by numerical derivation of $g(r,\lambda)$. It was shown[178,181] that the second-order term thus obtained greatly improves the Barker−Henderson MCA result (eq 13). Incorporation of higher-order terms into expansion 17 from the Zhou procedure greatly improves the accuracy of the results;[180,182,183] the resulting third-order TPT obviously overperforms the second-order MCA-TPT.[182] The outstanding performance of the third-order TPT continues even for derivative properties, such as the constant volume excess heat capacity.[184] Instead, other existing TPT versions provide only qualitative accuracy, at best, for derivative properties. The third-order TPT generally also shows[182] greater accuracy than other liquid state theories, including the well-known self-consistent Ornstein−Zernike approximation (SCOZA) and the HRT. In particular, whereas both the SCOZA and the HRT will run into numerical trouble for short-ranged potential, the Zhou procedure is free from any numerical drawback. The fifth-order version of the theory was also implemented[180] and was found to be a little more accurate than the third-order version. In ref,[180] a numerical procedure was advanced which, in the framework of the DFT formalism, allows an extension of the uniform TPT to nonuniform fluid situations. In the numerical procedure, a simple analytical approximation for the bulk second-order direct correlation function (DCF) was proposed. As a result, the numerical procedure does not require a numerical solution of the Ornstein−Zernike (OZ) equation.

In Zhou's version, although the expansion parameter λ is set to be 1 in the final expression for the full potential $u(r)$, the perturbative terms are still proportional to the value of β, and therefore, Zhou's TPT version is also more appropriate for high temperatures than for low temperatures. In fact, for sufficiently low temperatures, neither Zwanzig's nor Zhou's perturbation expansions will converge at all. An illustrative example of the divergent behavior occurring at extremely low temperature may be found in ref 180, where an unusual sharp increase in the absolute value of the derivative $\partial^{n-1}g(r,\lambda)/\partial\lambda^{n-1}|_{\lambda=0}$, involved in eq 18, for $n = 4$ and 5, was reported. In fact, the low temperature problem is inherent to all liquid state theories. Recently, one of the present authors has tried[185,186] a nonhard sphere TPT within the framework of the CPE by including part of the tail of the potential into the reference part. Extensive calculations indicate that the nonhard sphere TPT based on the CPE displays excellent performance even for situations of extremely short potential range and hence extremely low temperature, whereas various integral equation theories and the second-order MCA-TPT fail completely under these extreme situations.

II.8. Other Perturbation Theories for Simple Systems

The γ-Expansion

For potentials with short-ranged repulsive and long-ranged weakly attractive interactions, Hemmer[187] developed the so-called *γ-expansion*, further extended by Lebowitz et al.[188] They consider intermolecular potentials of the form

$$u(r) = u_0(r) - \gamma^3\varphi(\gamma r) \tag{19}$$

where γ^{-1} is a measure of the range of the attractive interactions. For a potential of this form, Hemmer develops a generalized cluster expansion which leads to the expression of the excess free energy and the radial distribution function as a power series of γ. The terms in the series can be obtained from the rdf of the reference system. The *γ-expansion* is useful for the study of systems with Coulombian interactions, but it is not useful for fluids without long-ranged interactions. Detailed and excellent accounts of the *γ-expansion* can be found in refs 3−6 so that there is no need here for going further in its analysis.

The Solvation Approximation

Very recently, Adib[189] has developed a simple procedure to obtain the first-order perturbative contribution $g_1(r)$ to the rdf of fluids with discrete potentials. The author expresses this quantity in the form

$$g_1(r) \approx -\beta g_0(r)[u(r) + \rho \int \mathrm{d}\mathbf{r}'\, u(r')\, \Delta g_0(\mathbf{r}'|\mathbf{r})] \tag{20}$$

where $\Delta g_0(\mathbf{r}'|\mathbf{r}) = g_0(\mathbf{r}'|\mathbf{r}) - g_0(\mathbf{r}')$ is the change in the local structure of the reference fluid at position $\mathbf{r}'$ from a given particle, due to the presence of another particle at position $\mathbf{r}$ from the same particle. To determine this quantity, the total perturbation energy is split into two contributions, one due to the particles 1 and 2, considered as the "solute" particles, and the other due to the remaining particles, considered as the "solvent" particles. When particles 1 and 2 are close enough, on switching on their contributions, considerable structural changes are induced in the solvent. When the quantity $\Delta g_0(\mathbf{r}'|\mathbf{r})$ is obtained from simulation in the reference HS system, the values of $g_1(r)$ obtained from the approximate eq 20, the solvation approximation, are in satisfactory agreement with the exact values of $g_1(r)$ obtained from simulation for SW, double SW, and LJ fluids at high densities. In the same paper, a simple and reasonably accurate procedure to obtain analytically $g_1(r)$ for step potentials based on excluded volume effects is proposed.

II.9. Equations of State and Radial Distribution Functions of the Reference Systems

The preceding theories, and others described below, require the knowledge of the rdf $g_0(r)$ of the reference system and the corresponding equation of state.

When the reference system is the hard-sphere fluid, a frequent choice for the rdf is the analytical expression arising from the Percus−Yevick theory.[190,191] However, as this expression is not sufficiently accurate, frequent use is made of the Verlet−Weis correction,[35] but there are available other analytical and very accurate expressions, such as the *rational function approximation*.[192,193]

Regarding the equation of state of the hard-sphere reference fluid, the most frequently used is the well-known Carnahan−Starling equation,[194] which is very simple and sufficiently accurate for most purposes.

In order to make easier the calculations in practical applications of the perturbation theories, several parametrizations of the rdf of the HS fluid have been proposed quite recently[195−197] based on the Percus−Yevick analytical solution. These results can be easily used to construct analytical expressions for the thermodynamic properties of fluids with different potential functions. Much earlier, simple parametrizations were proposed[198] for the integrals arising in perturbation theory in several kinds of potential interactions, based on the first few terms in the density expansion of the HS rdf and simulation data. These parametrizations were used recently in ref 55 to construct an analytical first-order perturbation theory for inverse-power and LJ-type potentials.

For some liquids, as in the case of liquid metals, other choices for the reference fluid, instead of the HS fluid, such as the soft-sphere fluid, are preferable. In this case, we need to resort to equations of state and structural functions for the reference fluid obtained from simulation data or from integral equation theory. However, this requires a greater computational effort than when using the HS reference system. An alternative strategy was developed by Ross[199] consisting in using a soft-sphere reference fluid whose free energy is determined using the rdf of the HS fluid.

For the equation of state of the hard-sphere reference solid, the Hall equation[200] is generally used. For the averaged rdf of the reference solid, several parametrizations based on the simulation data are available for the fcc[47,48,50,201,202] as well as for hcp[49,50] hard-sphere solids. Very recently, one of us,[43] extending the procedure outlined in ref 202, developed expressions for the rdf for the hard-sphere bcc and sc phases. It is to be noted that the latter two phases are unstable for the hard-sphere solid, so that the corresponding rdf cannot be obtained from simulations.

II.10. Perturbation Theories for Simple Fluid Mixtures

Several of the perturbation theories described for simple fluids have been applied also to simple fluids mixtures. For earlier reviews on the first achievements in the field, one can refer to refs 203 and 204. Now, instead of the interaction potential in eq 1, we will have for the interaction between particles i and j, which may belong to the same or different species,

$$u_{ij}(r,\lambda) = u_{ij}^{0}(r) + \lambda u_{ij}^{1}(r) \quad (21)$$

The reference system may be a monodisperse fluid or a multicomponent mixture. In the first case, the interaction potential $u_{ij}^{0}(r) = u_0(r)$ for every i and j. If the actual interaction potential $u_{ij}(r)$ for the mixture has a spherical hard core, the obvious choice for the reference system will be the hard-sphere fluid in the first case and a hard-sphere fluid mixture in the second case. In any case, the λ-expansion in eq 2 continues to be valid if we include within the term F_0 the contribution $NkT_i x_i \ln x_i$ of an ideal mixture, where x_i is the mole fraction of component i. The first-order contribution to the free energy is

$$\frac{F_1}{NkT} = 2\pi\rho \sum_{i} \sum_{j\neq i} x_i x_j \int_0^{\infty} u_{ij}^{1}(r)\, g_{ij}^{0}(r) r^2 \,\mathrm{d}r \; - \; 2\pi\rho \sum_{i} \sum_{j\neq i} x_i x_j d_{ij}^{2} g_{ij}^{0}(\sigma_{ij})(\sigma_{ij} - \delta_{ij}) \quad (22)$$

where σ_{ij} is the center to center distance for spheres i and j at contact in the HS reference system and δ_{ij} is an analogous effective distance in the actual system. In the case that the reference system is a monodisperse hard-sphere fluid, $g_{ij}^{0}(r) = g_0(r)$, the rdf of the HS fluid, and $\sigma = \sigma_{ij}$, the diameter of the spheres in the reference fluid, for every i and j, then choosing $\sigma = \sum_i x_i x_j \delta_{ij}$, the second term in eq 22 vanishes. In the case that the reference system is a hard-sphere fluid mixture, $g_{ij}^{0}(r)$ can be obtained from the Percus–Yevick solution for these mixtures.[205] For the equation of state, one can use the so-called Boublík–Mansoori–Carnahan–Starling–Leland (BMCSL) equation.[206,207] The perturbation series was carried out to second order for hard-core potential models in several ways[208,209] directly related to the BH procedures for pure fluids, with satisfactory results.

The theory was also extended to mixtures of Lennard-Jones molecules[210] by introducing an effective hard-sphere diameter for the interaction between particles of species i and j in a similar way as done previously for pure LJ fluids. However, the results were not satisfactory for these mixtures.[203] More recently, the effects of the nonadditivity of the perturbative tails, the size ratio, and the maximum depth ratio on the thermodynamic properties of mixing in LJ mixtures have been investigated[211] by means of first-order perturbation theory. The application of first-order perturbation theory to simple fluid mixtures in the last years includes the study of reentrant miscibility in binary mixtures of spherical molecules with short-ranged SW interactions between unlike species[212] and the calculation of the thermodynamic properties of He–H_2 mixtures.[213]

The WCA theory also was extended to simple fluid mixtures,[214] using a hard-sphere mixture as the reference system, with results satisfactory, on the whole, for the total thermodynamic properties but only moderately satisfactory for the excess properties, which are very sensitive to the accuracy of a theory. Further improvements have been proposed,[215–217] on the basis of different choices for the reference and perturbation potentials, or by using better choices for the diameters of the hard spheres of the reference system and for the equation of state of the reference hard-sphere mixture.[218] In the latter reference, a new criterion was used to determine the reference diameters in the mixture in such a way that the first-order term in the blip expansion of the excess free energy of the reference mixture around that of an additive hard-sphere mixture vanishes exactly. Moreover, to improve the accuracy of the Percus–Yevick radial distribution functions of the HS reference mixture, the Ornstein–Zernike equation was solved with distribution functions including a parameter that was determined from the condition that the EOS of the HS mixture equals that given by the BMCSL equation. The importance of properly treating the first-order term in the blip expansion used in the WCA theory was discussed in ref 219. The adequacy of different mixing rules to predict Henry constants in real mixtures of simple molecules by means of a WCA-type theory was tested in ref 220.

Another improvement consisted[221] in using a nonadditive hard-sphere reference system (NAHS), which is particularly appropriate for strongly nonadditive systems, such as certain molten alloys. The thermodynamic properties of the NAHS fluid in turn can be obtained from a recently proposed[222] perturbation theory which uses as the reference system an additive hard-sphere fluid mixture.

In some situations, as in the case of colloidal dispersions, some degree of polydispersity may be present. An expression for the free energy of a polydisperse hard-sphere mixture has been obtained[223] as a perturbative expansion in power series of the degree of polydispersity, derived from the BMCSL expression for the free energy.

On the other hand, the equation of state for monocomponent solids derived in ref 51 on the basis of the WCA theory was used quite recently,[224] in combination with an appropriate perturbation theory for the fluid, to successfully correlate the solid–liquid equilibria of argon/krypton and argon/methane mixtures as well as the solid–solid equilibria and the eutectic temperature of argon/methane mixtures.

The variational perturbation theory is another pure fluid theory that is readily extended to mixtures and provides satisfactory results for LJ mixtures.[225–228] This theory has been applied recently[229] to obtain analytical expressions for the thermodynamic properties of He–H_2 mixtures on the basis on an analytical parametrization of the rdf for the reference HS fluid.

Another perturbative approach for mixtures is related to the *conformal solution theory*. This theory applies to mixtures whose components interact with each other by means of potentials of the form

$$u_{ij}(r) = \varepsilon_{ij}\, f\left(\frac{r}{\sigma_{ij}}\right) \quad (23)$$

Taking as the reference fluid an ideal mixture with potential conformal with that of eq 23 with parameters ε_x and σ_x, and expanding the free energy of the mixture around the reference ideal solution in terms of suitable combinations of the parameters ε_{ij} and σ_{ij} raised to arbitrary powers, a family of second-order perturbation theories was obtained.[230] By properly choosing the reference fluid parameters ε_x and σ_x, the first-order term in the expansion vanishes, and neglecting higher-order terms, a zero-order perturbation theory for conformal mixtures results that, in particular, reduces to the van der Waals one-fluid theory (vdW1).[231] More details on these theories can be found in ref 203. Further refinements and applications of the vdW1 and other one-fluid theories can be found in refs 232–236.

The vdW1 theory continues to be a very popular one, as is computationally very simple and for some mixtures provides an accuracy comparable with that of other more complex perturbation theories. In particular, the vdW1 theory has been extensively used to calculate the monomer contribution within the statistical association fluid theory for complex fluids.[98,110,121,124,237]

A hybrid approach was developed in ref 238 for mixtures of fluids with discrete potential models. The procedure consists in using a hard-sphere fluid mixture for the reference fluid and a vdW1 approximation for the perturbation, whose contribution was determined from a parametrization previously developed[27] on the basis of the HTSE.

We will finish this subsection by mentioning the effective one-component fluid approach for colloidal suspensions. In this approach, the effect of the solvent is treated as an effective interaction acting between the solute particles (see ref 239 and references therein for more detailed explanations), and the thermodynamic properties and phase equilibria of the solute can be obtained from any suitable perturbation theory. The approach is commonly used in very asymmetric mixtures of hard spheres. Thus, first-order perturbation theory was used[240] to study the phase diagram in such kinds of mixtures considering different possible choices for the depletion potential between the large spheres due to the presence of the smaller ones. The theory predicted a complex phase behavior, including solid−fluid and fluid−fluid demixing and isostructural solid−solid transitions. In ref 241 the effective one-fluid approximation, in combination with a λ-integration obtained from simulation data, was used to obtain the phase diagram of asymmetric binary mixtures of hard-spheres with different diameter ratios. A similar procedure was used in ref 242 to analyze the phase behavior of colloid polymer mixtures using the Asakura−Oosawa depletion potential for the effective one-component fluid. The effective one-fluid approximation in combination with second-order BH perturbation theory was used[243] to study the phase behavior of star-polymer−colloid mixtures. Frequently, the depletion interactions in colloidal suspensions are modeled by a short-range potential such as the hard-core Yukawa potential. The reliability of this approximation to determine the solid−fluid transition was analyzed recently by one of us,[244] using a first-order perturbation theory for the solid and a semiempirical analytical perturbation theory for the fluid.[245] It was found that, to obtain the phase diagram, different short-ranged potential models can be replaced by each other upon the condition that they give the same values of the second virial coefficient.

The reliability of the effective one-component description of realistic colloidal and polymeric suspensions was analyzed in ref 246. It was shown that, contrarily to the cases of ordinary fluids, because of the effect of nonadditivity of the hard-core diameters for unlike interactions, in many cases the attractive depletion forces may be dominant for determining the structure and phase behavior. In fact, using a first-order perturbation theory in combination with an effective one-component approach for HS binary mixtures with moderate diameter ratios, it was concluded[247] that the presence of moderate nonadditivity may lead to the presence of a fluid−fluid critical point in the stable region of the phase diagram that, in absence of nonadditivity, will fall into the metastable region. On the other hand, the soft-core effective interactions between polymers in solution may lead to mean field behavior fluid. Therefore, one must be careful in determining the effective depletion potential and the choice of the theory to apply. Moreover, in real suspensions, attractive forces, in addition to the depletion forces, may be present.

The effect of the presence of solute−solvent and solvent−solvent short-range attractive forces was shown[248] to give rise to important changes in the phase diagram of the effective one-component fluid as compared to the case of purely hard-core interactions. The effective one-fluid approach was used together with the WCA perturbation theory to determine the thermodynamic properties and the phase diagram of a charged colloidal dispersion.[249]

The effective one-component approximation, and even conventional perturbation theory, may break down in colloid−polymer mixtures. In a recent paper,[58] a mixture consisting of hard-sphere colloids, with radius R_c, and self-avoiding polymer coils, with radius of gyration R_g, was considered. It was found that the effective one-component approach is reasonable in the colloidal regime, $R_c/R_g > 1$, provided that the ratio is large enough. In the protein regime, $R_c/R_g < 1$, the one-component picture is no longer applicable because of the importance of many-body interactions as compared with the effective pair interactions.[58] Instead, the system can be mapped onto an effective two-component system[58] with two reference fluids, one for the HS−HS interaction and the other for the polymer−polymer interaction considering the polymer coils as soft colloids, plus an effective HS−polymer interaction. Then a perturbation theory like that outlined in subsection II.1 in combination with the effective two-component system was shown to be applicable to any value of the ratio R_c/R_g.

II.11. The Virial Expansion

The virial expansion of the compressibility factor $Z = pV/NkT$

$$Z = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1} \tag{24}$$

where B_n is the n-th virial coefficient and $\rho = N/V$ is the number density, may be considered as a perturbative expansion of the equation of state using the ideal gas as the reference system and the density as the parameter. As is well-known, the virial coefficients can be conveniently expressed in terms of the so-called *cluster diagrams* in a way which is increasingly complex with increasing n. The essentials of the calculation of the first few virial coefficients can be found in any textbook on Statistical Physics, so that there is no need to give here further details. We will restrict ourselves to give a quite detailed account of the state of the art of the theoretical calculation of the virial coefficients of fluids with model potentials. For convenience, we will group the different kinds of fluids into three categories, namely, pure hard-body (HB) fluids, hard-body fluid mixtures, and other kinds of pure fluids and mixtures.

Virial Coefficients for Pure Hard-Body Fluids

The first few virial coefficients have been determined for many hard-body fluids. The interested reader is addressed to ref 250 for an earlier review on the subject. The simplest HB fluid is the HS fluid, for which the virial coefficients B_n up to $n = 4$ are known exactly, whereas for $n \geq 5$ they need to be determined numerically from a Monte Carlo procedure. At present, the virial coefficients B_n for $5 \leq n \leq 10$ are known with great accuracy.[251,252] Frequently, the virial series of the HS fluid is used to obtain a closed form of the equation of state. To this end, Padé approximants are frequently used. These approximants are often also used to predict the virial coefficients beyond those "exactly" known. Recent estimates obtained in this way for the virial coefficients of the HS fluid for $n > 10$ can be found in refs 251−253.

For nonspherical convex hard-body fluids, only the second virial coefficients can be determined analytically as a function of geometrical parameters (see ref 250 for the calculation of B_2 for a number of these geometries). The exact second virial coefficient for hard ellipsoidal fluids (whose convex molecules have three distinct principal axes) was determined quite recently.[254] For nonconvex hard-body molecular fluids, in general, even the second virial coefficient cannot be calculated exactly but for a few cases. For many HB fluids, either having convex or nonconvex molecules, several virial coefficients B_n, in general with $n \leq 5$, have been obtained numerically from a Monte Carlo procedure (see the cited ref 250 and references therein for a review of the achievements in this field before 1986). More recently, an exact analytical expression has been obtained[255] for the second virial coefficient of linear homonuclear rigid chains consisting of hard spheres. The virial coefficients for $3 \leq n \leq 5$ were determined for hard prolate[256] and oblate[257] spherocylinders with different geometries. The values of B_3 to B_5 for prolate and oblate hard ellipsoids of revolution with different geometries were reported in ref 258, those from B_3 to B_7 were reported in ref 259, and those for hard ellipsoidal molecules were reported in ref 260 from B_3 to B_5. For cut spheres with several aspect ratios, the values of B_2 to B_5 are available in ref 261. The virial coefficients of rigid linear homonuclear molecules consisting of different numbers of equal spheres and with different center-to-center distances have been reported by different authors[262−265] for $n \leq 5$. For rigid diatomic and triatomic linear heteronuclear molecules as well as for rigid nonlinear molecules that are either homonuclear or heteronuclear, these virial coefficients have also been determined for different geometries.[262] The virial coefficients B_2 to B_6 are available for prolate and oblate hard Gaussian overlap fluids.[266,267] Quite recently, the virial coefficients B_6 to B_8 for hard ellipsoids of revolution, hard spherocylinders, and cut spheres with different geometries have been reported.[268] These models can be used as reference systems in perturbation theories for models of real molecular fluids.

For a hard core model of carbon tetrachloride, B_2 to B_4 have been calculated.[269] B_2 has been determined[270] for hard tetrahedral molecules with different geometries. The virial coefficients B_2 to B_5 have also been determined[271] for several pseudohard reference models (fused hard-sphere models with embedded sites of different kinds) of water, methanol, and ammonia.

For hard models of polyatomic molecules having different molecular conformations, the calculation of the virial coefficients is much more cumbersome. The virial coefficients B_2 to B_5 for hard models of several *n*-alkanes were reported in ref 272, and the second virial coefficients of different linear and branched hard alkane models were reported in ref 273. For a hard model of a polymer with with fixed bond angle and discretized torsional angles, B_2 to B_4 have been determined for different values of m.[274]

For flexible chains made up of hard monomers, the calculation of the virial coefficients is still more complex. For freely joined chains, the second virial coefficient has been determined for different numbers m of monomers in the chain,[275] and more recently B_2 to B_4 have been determined.[264] The effect of the flexibility on the virial coefficients B_2 to B_4 of chains made of tangent hard spheres was analyzed in ref 276.

Virial Coefficients for Hard-Body Fluid Mixtures

The partial contributions to several virial coefficients have been determined for different hard-body fluid mixtures (mainly hard-sphere mixtures). Some results can be found in the cited review.[250] Let us take a quick look at this point.

Mixtures of Additive Hard Spheres. The second and third virial coefficients of a binary mixture of additive hard spheres with different sizes are known analytically.[277,278] The partial contributions to the fourth,[279−281] fifth,[280−283] and sixth[281,283] virial coefficients have been determined numerically for different values of the diameter ratio and the seventh virial coefficient has been reported for the size ratio $R = 10$.[281]

In addition, a procedure to obtain approximate, though very accurate, analytical expressions for the virial coefficients was proposed in ref 284, and the explicit expressions for B_4 to B_7 obtained from this method are available.[239,285] Another procedure, equally accurate, was developed in ref 286, and explicit expressions were provided for coefficients B_4 and B_5.

On the other hand, in ref 287, explicit expressions for the averaged second and third virial coefficients of a polydisperse mixture of hard spheres were provided and the dependence of the higher order virial coefficients on the moments of the size distribution was analyzed.

Mixtures of Nonadditive Hard-Spheres. The second and third virial coefficients for mixtures of nonadditive hard spheres are analytical, and their expressions have been known for a long time[288] (see also ref 278). The partial contributions to B_4 and B_5 for different diameter ratios and different nonadditivities have been reported by different authors.[281,289−291]

Other Hard-Body Mixtures. The available numerical calculations of the virial coefficients for HB mixtures of nonspherical particles are very scarce. B_2 to B_4 were calculated for a number of mixtures of hard-dumbbells.[292] Much more recently,[293] B_2 to B_5 for mixtures of the same kind of molecules with different center to center distances were calculated.

In a very recent paper,[294] second virial coefficients have been determined for mixtures of hard spheres and pseudohard bodies mimicking the short-range repulsive interactions in water.

To end this topic, it is worth mentioning here the analysis performed in ref 295 on the virial coefficients B_2 to B_4 of a hard model of a chiral molecule as well as those of the racemic mixture. No differences were found between the virial coefficients of the chiral molecule and those of the racemic mixture.

Virial Coefficient for Fluids and Fluid Mixtures

A number of virial coefficients have been determined for different fluids with other than purely hard-body interactions. In some cases, several of the virial coefficients can be obtained in an analytical way either directly or by means of an inverse temperature expansion. Let us summarize the state of the art for a number of potential models.

Square-well potential. B_2 to B_5.[268,296−300]
Triangular-well potential. B_2 to B_4.[301]
Inverse power potentials. B_2 to B_7.[296,302,303]
Sutherland. B_2 to B_3.[304−306]
Lennard-Jones potential. B_2 to B_5.[296,307−310]
Kihara. B_2.[296,311]
Polar rodlike molecules. B_2.[312]
Dipolar hard sphere fluids. B_3.[313]
Lennard-Jones with association sites. B_2[314]
Homonuclear and heteronuclear square-well diatomics. B_2 and B_3.[315−317]
Square-well chain molecules. B_2.[318]
Quadrupolar Lennard-Jones diatomics. B_2 to B_4.[319−321]
Water models. B_2 to B_6.[322]

III. Progress in Perturbation Approaches to Solve the Ornstein−Zernike Equation

A way to solve the Ornstein−Zernike equation with several closures consists in using perturbation procedures. However, perturbation approaches to solve the Ornstein−Zernike equation are not new. The ORPA and related approximations, also cited in the same section, can be considered from this viewpoint. In general, the approaches for solving integral equation theories consisting in splitting the intermolecular potential into a reference potential plus a perturbation may be considered as belonging to that category. This is the case of the so-called *corrected integral equations*[323] and other related approximations.[324] But the use of perturbation procedures in conjunction with integral equation theories can be tracked back to the work of Lado,[325] later extended by the same author,[326] whose results, and other similar approaches, are referred to as *reference integral equation theories*.[327] All these theories have in common that they use in one way or another the known results for the reference system. Next, we will summarize the foundations of this kind of theories and the progress in this field.

III.1. Corrected Integral Equation Theories

A method to improve the results provided by integral equation theories was developed by Madden and Fitts,[324] and a closely related procedure was derived by Smith ad Henderson,[323] who denoted this kind of approximations, based on the use of known results for the reference system, as *corrected integral equations*.

The starting point in the Madden and Fitts procedure is to consider a potential function of the form of eq 1 and the corresponding series expansion for the rdf given by eq 6. The derivatives in the latter equation can be approximated by those obtained from the rdf $g^{\mathrm{IE}}(r)$ provided by a particular integral equation theory (IE), with the result

$$g(r,\lambda) \approx g_0(r) + \sum_{n=1}^{\infty} \left.\frac{\partial^n g^{\mathrm{IE}}(r,\lambda)}{\partial \lambda^n}\right|_{\lambda=0} \frac{\lambda^n}{n!} \tag{25}$$

If we replace in this series $g_0(r)$ by $g_0^{\mathrm{IE}}(r)$, we will obtain the series expansion of $g^{\mathrm{IE}}(r)$. Then, subtracting the two series, the final result is

$$g(r,\lambda) \approx g_0(r) + g^{\mathrm{IE}}(r) - g_0^{\mathrm{IE}}(r) \tag{26}$$

which is a compact version of eq 25. It is obvious that the improvement introduced by this procedure relies on the improved accuracy of $g_0(r)$ with respect to $g_0^{\mathrm{IE}}(r)$.

A convenient feature of this procedure is that each of the perturbative terms in the approximate expansion in eq 25 is related to the previous terms in the expansion and can be obtained from an iterative solution of the IE theory. This, in turn, allows us to obtain the corresponding terms in an approximate expansion for the free energy similar to eq 2.

Smith and Henderson[323] denote the preceding kind of approximations as *hybrid theories* and reserve the term *corrected theories* for those resulting from a procedure closely related to the former, consisting in splitting the total and direct correlation functions into the contributions from the reference system and the perturbation, namely

$$h(r) = h_0(r) + h_1(r) \tag{27}$$

$$c(r) = c_0(r) + c_1(r) \tag{28}$$

Inserting the two last equations into the Ornstein−Zernike equation gives an integral equation which can be solved provided that we know the total $h_0(r)$ and direct $c_0(r)$ correlation functions for the reference system and we introduce an approximate relation between $h_1(r)$ and $c_1(r)$. There are subtle differences between the ordinary, hybrid, and corrected IE theories. These differences are analyzed in detail in ref 323.

III.2. Reference Integral Equation Theories

Let us consider the exact closure condition for the Ornstein−Zernike equation

$$c(r) = h(r) - \ln y(r) + B(r) \tag{29}$$

where $y(r) = g(r) \exp[u\beta(r)]$ is the cavity function and $B(r)$ is the so-called bridge function. If the bridge function were exactly known, we could exactly solve the OZ equation, but this is not the case in general. Introducing different approximations for these functions, we obtain different approximate closures, giving rise to different integral equation theories. When considering a potential of the form of eq 1, the correlation functions and the bridge function will separate into two contributions, one corresponding to the reference fluid and the other to the perturbation. The procedure developed by Lado[325,326] consists in considering the exact closure (eq 29) for the reference system and an approximate one for the perturbation. This procedure leads to the so-called *reference integral equations*.[327] The reason for doing so is that, whereas the bridge function is not exactly known for the whole potential, if we use the HS fluid as the reference system, accurate estimates for its bridge function are available from simulations as well as an accurate analytical expression.[328]

Perhaps the most widely used of this kind of theories is the *reference hypernetted chain* (RHNC) theory, in which the bridge function is retained in eq 29 for the reference fluid but neglected in the perturbation contribution. From the viewpoint of eq 5 for the free energy, the RHNC consists in retaining the function $B_0(r)$ of the reference system, corresponding to $\lambda = 0$, for any value of λ. This approximation is justified by the *universality of the bridge function* pointed out by Rosenfeld and Ashcroft.[329] The approximation is completed with suitable optimization conditions for the choice of the reference system. In the case that the potential of the reference system depends only on a single length parameter σ, as is the case of the hard-sphere system, the optimizing condition is[330]

$$\rho \int \mathrm{d}\mathbf{r}[g(r) - g_0(r)]\sigma \frac{\partial B_0(r)}{\partial \sigma} = 0 \tag{30}$$

In the case that the reference potential depends on an energy parameter ε in addition to a length parameter, a condition similar to eq 30 is imposed on ε. The theory provides very satisfactory results for fluids with a variety of intermolecular potentials that are either short-ranged or long-ranged. In fact, this theory is often used to correct for the long-ranged interactions in simulations with Coulombic potentials.[331] An efficient method to solve the RHNC equation for simple fluids was developed by Lomba.[332] The influence of different conditions for thermodynamic consistency on the results provided by the RHNC has been analyzed quite recently.[333] A new route to obtain the thermodynamic properties of LJ fluids within the framework of the RHNC theory has been recently proposed by one of us.[334]

The RHNC theory has been extended to molecular fluids[335,336] using a bridge function $B_0(12)$ appropriate for the hard diatomic molecules of the reference fluid.[337,338] This theory is referred to as RHNC-VM and provides satisfactory accuracy for homo- and heteronuclear diatomic molecules that are either polar or nonpolar.

The RHNC procedure has also been extended to mixtures of molecules of charged hard spheres, using for the reference system a mixture of hard spheres of unequal diameters. For the rdf's of the hard-sphere reference mixture, an extension to hard-sphere mixtures[214] of the Verlet−Weis expression for monodisperse hard spheres[35] has been used.[339] A similar procedure was used[340] for Lennard-Jones mixtures within the framework of the optimized RHNC theory.

This theory has proven to be accurate too for predicting the structure and phase behavior of very asymmetric binary mixtures of hard spheres treated in the effective one-component approach.[248] This is particularly remarkable because of the short-range of the attractive depletion forces in this situation. A crucial point in the one-component approach is to determine the potential of the mean force acting on the solute particles at infinite dilution due to the presence of the solvent particles. This may be achieved by computer simulations. An alternative procedure consists in using the rdf of the solute particles at infinite dilution by using a suitable integral equation. To this end, again the RHNC theory with bridge functions $B_{ij}(r)$ obtained from the fundamental measure theory[341] may be useful.[342,343] This procedure has been quite successfully applied to confined colloids.[344−346]

III.3. Perturbative Solutions of the Mean Spherical Approximation

Another kind of perturbative solution of the Ornstein−Zernike equation has been developed by Tang and Lu[347,348] within the context of the mean spherical approximation (MSA). The starting point is the expression of the total $h(r)$ and direct $c(r)$ correlation functions as series expansions in terms of a suitable parameter ε in the form

$$h(r) = h_0(r) + \varepsilon h_1(r) + \varepsilon^2 h_2(r) + ... \tag{31}$$

$$c(r) = c_0(r) + \varepsilon c_1(r) + \varepsilon^2 c_2(r) + ... \tag{32}$$

where the subscript 0 refers to the hard-sphere reference system and subscripts i refer to the ith perturbative contributions. Combining these expressions with the Ornstein−Zernike equation, these authors developed a general procedure, within the framework of the mean spherical approximation, to obtain the radial distribution function for fluids with a hard spherical core potential as a sum of contributions in the form

$$g(x) = \sum_{i=0}^{\infty} g_i(x) \tag{33}$$

where $x = r/\sigma$ is the reduced distance. The procedure lead to analytical expressions for the zero- and first-order contributions in expression 33 for a number of potential models of the above-mentioned kind,[348,349] giving rise to accurate results for the thermodynamic and structural properties.[349,350] The theory also provides analytical expressions for the direct correlation function $c(r)$, which is particularly useful in the study of inhomogeneous fluids, for different kinds of intermolecular potentials.[351,352] The procedure has been successfully extended to mixtures of fluids interacting by means of spherical hard-core potentials.[353]

Analytical expressions up to fifth order in an inverse temperature expansion of the energy and the rdf at contact for hard-core Yukawa (HCY) fluids obtained on the basis of the MSA were reported in ref 354 and later used[355] to analyze the thermodynamic properties and phase equilibria HCY fluids with different ranges.

A novel perturbative solution of the MSA has been proposed very recently for the hard-core Yukawa fluid.[356] It is based on the use of another hard-core Yukawa fluid with a shorter range as the reference system. The structure of the reference system is also determined from the MSA. The structure factor thus obtained for the whole system performs much better than that obtained either using for the reference system the HS one or solving directly the MSA for the whole system.

IV. Progress in the Perturbation Approach for Constructing the Density Functional Approximation

As a powerful computational tool for inhomogeneous phenomena, the classical density functional theory (DFT)[357] has experienced a huge development in the past 20 years, and the perturbation approach also plays an important role in this field. A recent review by Wu[358] on density functional theory includes some comments on the application of perturbation procedures in combination with the DFT formalism. The most essential quantity in the DFT is the excess Helmholtz free energy $F_{\mathrm{ex}}([\rho(r)])$ expressed as a functional of the density distribution $\rho(r)$. As the exact expression for the functional is never known, most theoretical activity in the field is invested in devising appropriate approximations for $F_{\mathrm{ex}}([\rho(r)])$ or its first-order functional derivative: the inhomogeneous first-order direct correlation function (DCF) $c^{(1)}(\mathbf{r},[\rho])$. In this regard, the approximation was first developed for the hard sphere fluids, and later, various density functional approximations (DFA) were proposed for general van der Waals fluids. We will first discuss the DFA for the hard-sphere system and then the DFA for other systems. As the present review is focused on perturbation approaches in liquid state theory, development of nonperturbation approaches in DFT will be skipped over. These developments include the weighted density approximation (WDA)[359] and the fundamental measure functional (FMF).[360] For a detailed account of these approximations, the interested readers are referred to ref 361.

IV.1. Density Functional Approximation for Hard Spheres

Freezing

The pioneering work of Ramakrishnan and Yussouff (RY)[362] on application of the DFT approach to the freezing of the hard-sphere fluid is based on a functional perturbation expansion of a solid phase $F_{ex}([\rho])$ around the liquid phase coexistence density truncated at second order. The expansion can be extended in a straightforward manner to third order,[363] but the predicted coexistence conditions are much worse than those of the second-order version. This fact indicates that the convergence of the perturbation expansion for the solid phase $F_{ex}([\rho])$ is not fast enough. Haymet and Oxtoby[364] have shown that, at least for the hard-sphere solid phase, the third-order term can be approximated by its value at zero wave vector, because the nonzero wave vector contributions tend to cancel each other; this discovery is exploited[365] in subsequent DFT investigations about freezing of non-hard-sphere systems. In particular, the RY theory and its later formulation were extended to investigating the freezing of hard polymer chains.[366]

Inhomogeneous Liquid Phase

Although not sufficiently operative for the solid phase, the functional perturbation expansion (FPE) has obtained enormous success for the inhomogeneous liquid phase, for which it is considered that the third-order term is necessary to achieve better performance of the FPE approximation.[367] The FPE is usually operated in either of two ways; one is to expand $F_{ex}([\rho])$ itself; the other is to expand the nonuniform first-order DCF $c^{(1)}(\mathbf{r},[\rho])$. In any case, the n-th-order term in the expansion depends on the n-th-order bulk direct correlation function. Based on symmetrical and intuitive considerations, a simple form of the third-order bulk DCF was proposed[368] for use in the third-order FPE approximation, in the form

$$c_0^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = B\int d\mathbf{r}_4\, a(\mathbf{r}_4 - \mathbf{r}_1)\, a(\mathbf{r}_4 - \mathbf{r}_2)\, a(\mathbf{r}_4 - \mathbf{r}_3) \quad (34)$$

Here

$$a(r) = \frac{6}{\pi\sigma^3}H\left(\frac{\sigma}{2} - r\right) \quad (35)$$

or

$$a(r) = (1 - x^2/\sigma^2)H(|\sigma - x|) \quad (36)$$

where $H(r)$ is the Heaviside step function. One adjustable parameter B enters into the expression of $c_0^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$, which has to be specified in practical DFT calculations. The approximation in eq 34 was employed to study hard-sphere and Lennard-Jones fluids,[368] square-well fluids,[369] the sticky hard-sphere fluid,[370] and Yukawa fluids[371] in the perturbation DFT framework, where the third-order FPE approximation was used for the tail contribution and various WDA recipes for the hard-sphere contribution. It has been shown[372,373] that with the needed bulk second-order DCF given by the mean spherical approximation, as done in ref 371, terms higher than second-order in the FPE of the tail contribution are exactly zero, and the reason for the partial success[371] of the kernel function-based third-order FPE approximation for the tail contribution is due to the adjustable parameter B and the short-range of the kernel function. The approximation in eq 34 was extended to binary hard-sphere mixtures,[374] and the resulting third-order perturbation DFT approach was shown to perform satisfactorily for the inhomogeneous binary hard-sphere mixture. Obviously, approximation 34 employs the same kernel function for different interaction potentials or different parts of the interaction potentials, so that specific information for particular potential functions is not reflected in the approximation. An analytical expression for the n-th bulk DCF, which only needs the bulk second-order DCF as input, was derived[375] from a simple weighted density approximation. This general analytical expression reduces to the same functional form as in eq 34 for the bulk third-order DCF, but the corresponding kernel function is replaced by the bulk second-order DCF and the adjustable parameter is exactly expressed by a quantity involved with space integration of the bulk second-order DCF. The bulk third-order DCF has ben successfully employed to calculate analytically the three-body correlations in the mixed state of type-II superconductors.[376]

The biggest merit of the FPE is its computational simplicity, a point that becomes even more obvious for the case of mixtures. However, its accuracy depends strongly on the accuracy of the bulk high-order DCFs. We will return to this point with more detail when discussing the DFA for non-hard-sphere systems in subsection IV.2.

Hard-Sphere Bridge Density Functional Approximation

The bridge density functional approximation (BDFA) for an inhomogeneous hard sphere fluid is also based on expanding $c^{(1)}(\mathbf{r},[\rho])$ around the coexistence bulk density ρ_b:

$$c^{(1)}(\mathbf{r};[\rho]) = c_0^{(1)}(\rho_b) + \int dr_1(\rho(\mathbf{r}_1) - \rho_b)c_0^{(2)}(|\mathbf{r} - \mathbf{r}_1|;\rho_b) + \sum_{n=3}^{\infty}\frac{1}{(n-1)!}\int dr_1\int dr_2 ... \int dr_{n-1}\prod_{m=1}^{n-1}[\rho(\mathbf{r}_m) - \rho_b]c_0^{(n)}(\mathbf{r}, \mathbf{r}_1, ..., \mathbf{r}_{n-1};\rho_b) \quad (37)$$

Here, $c^{(1)}(\mathbf{r},[\rho_b])$ is the uniform counterpart of $c^{(1)}(\mathbf{r},[\rho])$ and $c_0^{(n)}$ is the bulk n-th DCF; each functional derivative, i.e. the expansion coefficient $c_0^{(n)}(\mathbf{r},\mathbf{r}_1,...,\mathbf{r}_{n-1};\rho_b)$, $n \geq 2$, is evaluated at ρ_b. Based on the “universality” of the free energy density functional, i.e. the functional form of $F_{ex}([\rho])$ is not dependent on the external potential responsible for the formation of the density distribution $\rho(\mathbf{r})$, and the fact that the uniform bulk fluid is a particular kind of inhomogeneous fluid, it was proved[377] that the sum in eq 37 can be represented by a so-called bridge functional which however has to be expressed as a function of the second term on the right side of eq 37, i.e.

$$c^{(1)}(\mathbf{r};[\rho]) = c_0^{(1)}(\rho_b) + \int \mathrm{d}\mathbf{r}_1(\rho(\mathbf{r}_1) - \rho_\mathrm{b})\, c_0^{(2)}(|\mathbf{r} - \mathbf{r}_1|;\rho_b) + B\left(\int d\mathbf{r}_1(\rho(\mathbf{r}_1) - \rho_\mathrm{b})\, C_0^{(2)}(|\mathbf{r} - \mathbf{r}_1|;\rho_b)\right) \quad (38)$$

here, the bridge function B is exactly the one which, in combination with the OZ integral equation, results in the bulk second-order DCF $c_0^{(2)}$. Extension of the BDFA to a binary hard sphere mixture is straightforward.[378,379] The BDFA and the FMF have been used[380] to study inhomogeneous penetrable spheres with bounded interactions, with the result that at low temperature the FMT functional is superior to the BDFA and compares well with the computer simulation results, whereas at high temperature the BDFA provides better performance than the FMT functional.

Lagrangian Theorem-Based DFA for the Inhomogeneous Hard-Sphere Fluid

We can make use of the Lagrangian theorem of differential calculus and apply the functional counterpart of the theorem to the FPE of $c^{(1)}(\mathbf{r},[\rho])$ or $F_{\mathrm{ex}}([\rho])$ in the DFT of interest. The outcome is that one obtains the full physics at the lowest truncation of the FPE. Consequently, an associated parameter results that is specified by statistical mechanics sum rules. Implementation of the above idea in $c^{(1)}(\mathbf{r},[\rho])$ leads to a so-called Lagrangian theorem-based density functional approximation (LTDFA)[381] for the inhomogeneous hard sphere fluid, and different sum rules lead to different values of the associated parameter. A simple hard wall sum rule gives for the parameter a value close to 0.5,[381] while another sum rule ascertains the parameter value to be exactly equal to 0.5.[382] The implementation of the procedure in $F_{\mathrm{ex}}([\rho])$ was also carried out.[383] Extension to a binary hard sphere mixture is straightforward,[384] and the prediction accuracy is acceptable. A desirable character of the LTDFA[381] is its self-correction capability,[385] which perhaps devitalizes the harmful outcome arising from a poor accuracy of the second-order bulk DCF used as input. This character directly leads to a kind of LTDFA for polymer formed by hard sphere chains.[386] Using a procedure similar to that underlying the LTDFA,[381] a new WDA approach for inhomogeneous fluids was developed[387] which was shown to be appropriate for hard-sphere and Lennard-Jones fluids in confined geometries. The application of the LTDFA[381] to general van der Waals fluids will be discussed in subsection IV.2.

IV.2. Density Functional Approximation for General Inhomogeneous van der Waals Fluids

The developments in the case of non-hard-sphere DFAs largely lag behind those for the hard-sphere DFAs. Until several years ago, the most generally employed DFAs for general inhomogeneous van der Waals fluids were still crude van der Waals mean field approximations (MFA) with varied degrees of sophistication. Only in recent years, were several novel non-hard-sphere DFAs advanced by different authors, bringing new expectations for improving accuracy. Currently, the perturbation approach predominates over DFAs for general van der Waals fluids. There exist different kinds of implementations with different degrees of numerical complexity and accuracy. We will describe the developments in this field by following the time sequence in which these methods were advanced.

van der Waals Mean Field Approximation

The interaction potentials in van der Waals fluids usually consists of a highly repulsive term at short interparticle separations and a weakly attractive part at larger interparticle separations. Although the $F_{\mathrm{ex}}([\rho])$ can be expressed exactly as[357]

$$F_{\mathrm{ex}}([\rho]) = \frac{1}{2}\int\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\rho(\mathbf{r})\,\rho(\mathbf{r}')\,u(\mathbf{r},\mathbf{r}')\int_0^1 \mathrm{d}\lambda\, g(\mathbf{r},\mathbf{r}';\lambda) \quad (39)$$

where $g(\mathbf{r},\mathbf{r}';\lambda)$ is the pair correlation function of the system with a density distribution $\rho(\mathbf{r})$ and a pair potential $u\lambda(\mathbf{r},\mathbf{r}')$. Some approximation is needed to proceed from eq 39 because little is known about $g(\mathbf{r},\mathbf{r}';\lambda)$. A common procedure underlying most DFT approximations is to separate the pair potential into a short-range repulsive part $u_0(\mathbf{r},\mathbf{r}')$ and a long-range attractive part $u_1(\mathbf{r},\mathbf{r}')$. Accordingly, $F_{\mathrm{ex}}([\rho])$ is composed of a repulsive term $F_0([\rho])$ and an attractive term $F_{\mathrm{per}}([\rho])$. The repulsive part is usually approximated by the hard-sphere potential with an effective diameter d; as a result, $F_0([\rho])$ can be replaced by the excess free energy functional of the corresponding inhomogeneous effective hard-sphere fluid. On the other hand, $F_{\mathrm{per}}([\rho])$ is now given by

$$F_{\mathrm{per}}([\rho]) = \frac{1}{2}\int\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\rho(\mathbf{r})\,\rho(\mathbf{r}')\,u_1(\mathbf{r},\mathbf{r}')\int_0^1 \mathrm{d}\lambda\, g(\mathbf{r},\mathbf{r}';\lambda) \quad (40)$$

If one assumes that

$$g(\mathbf{r},\mathbf{r}';\lambda) = H(|\mathbf{r} - \mathbf{r}'| - d) \quad (41)$$

then, combining eqs 40 and 41, one obtains the MFA for the long-range part,

$$F_{\mathrm{per}}([\rho]) = \frac{1}{2}\int\int_{|\mathbf{r}-\mathbf{r}\prime>d} \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\,\rho(\mathbf{r})\,\rho(\mathbf{r}')\,u_1(\mathbf{r},\mathbf{r}') \quad (42)$$

It was shown[388] that in case of the Lennard-Jones fluid near a hard wall the MFA is qualitatively incorrect at low densities and quantitatively inaccurate at intermediate and high densities. However, the MFA at least qualitatively describes[389] the first-order wetting and triple-point prewetting transitions of the model LJ fluid in the presence of attractive walls or neon on solid CO_2. This is possibly due to the fact that the strong attractive forces between the fluid particles and the wall overshadow the attraction between the fluid particles themselves and, as a result, the poor performance due to the MFA is not displayed.

Combining the Wertheim and the WDA treatment extending the bulk associative contribution to an inhomogeneous case, the MFA has been applied[390] to study a simple model of an associating Lennard-Jones fluid confined by slitlike pores with Lennard-Jones adsorbing walls. It has been found that the computer simulation density profiles are reproduced quite well by the resulting perturbation DFT. It may be that the satisfactory performance achieved is due to the combination of the accurate treatment of association and the strong attractive forces between the associating Lennard-Jones particles and the walls, which overshadows the inaccuracy of the MFA for the dispersion attraction between the associating Lennard-Jones particles. The MFA can be improved by replacing $g(\mathbf{r},\mathbf{r}';\lambda)$ by the pair correlation function $g_{\mathrm{hs}}(\mathbf{r},\mathbf{r}')$ of the effective hard-sphere system, which actually constitutes a formal extension of the bulk first-order TPT to inhomogeneous systems, that is

$$F_{\mathrm{per}}([\rho]) = \frac{1}{2}\int\int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\rho(\mathbf{r})\,\rho(\mathbf{r}')\,u_1(\mathbf{r},\mathbf{r}')\,g_{\mathrm{hs}}(\mathbf{r},\mathbf{r}') \tag{43}$$

As a general rule, the subsequent approximation is to substitute $g_{\mathrm{hs}}(\mathbf{r},\mathbf{r}')$ by its bulk counterpart, i.e. the bulk hard sphere rdf evaluated at some effective density $\tilde{\rho}$. Different specifications for $\tilde{\rho}$ define different improvements on the MFA. A simple recipe[391] is to assume $\tilde{\rho} = \rho[(\mathbf{r} + \mathbf{r}')/2]$ or $\tilde{\rho} = [\rho(\mathbf{r}) + \rho(\mathbf{r}')]/2$. A more reasonable and safe procedure[388] is to take $\tilde{\rho} = {}^{-}\rho[(\mathbf{r} + \mathbf{r}')/2]$ or $\tilde{\rho} = [\bar{\rho}(\mathbf{r}) + \bar{\rho}\mathbf{r}')/2]$, with $\bar{\rho}$ being the local density averaged over a sphere of appropriate radius. Following the same procedure, the bulk second-order MCA-TPT was also extended[388] to inhomogeneous systems, and the improvement over the MFA was remarkable. It is to be pointed out that all of the above approximations can be applied to the solid phase, with the only difference being that the simple local approximation $\tilde{\rho} = \rho[(\mathbf{r} + \mathbf{r}')/2]$ or $\tilde{\rho} = [\tilde{\rho}(\mathbf{r}) + \rho(\mathbf{r}')]/2$ will not work in the solid phase because $\rho(\mathbf{r})$ reaches values which are many times larger than the maximum allowed density in the uniform liquid. In fact, most of the correlation structure in the solid phase is already implicitly included[392] in the density product, so that the MFA performs well for solid phase perturbation free energy calculations.[393] As a result, $g_{\mathrm{hs}}(\mathbf{r},\mathbf{r}')$ should be almost a Heaviside step function. Correspondingly, the effective density ρ in the solid phase rdf mapping is expected to be very small. To achieve this requirement, the usual recipe for determination of the effective density in the inhomogeneous liquid phase certainly does not suit the solid phase situation, so that an alternative recipe has to be devised. By an exact local-compressibility relation, a position-dependent $\tilde{\rho}$ can be determined as follows[392]

$$\int \mathrm{d}\mathbf{r}'\,\rho(\mathbf{r}')[g^{r}(|\mathbf{r} - \mathbf{r}'|), \tilde{\rho}(\mathbf{r}) - 1] = -1 + \frac{kT}{\rho(\mathbf{r})}\frac{\mathrm{d}\rho(\mathbf{r})}{\mathrm{d}\mu} \tag{44}$$

where μ is the chemical potential. A simpler recipe may be obtained[394] using a constant effective density, which is obtained from the exact global compressibility equation

$$\frac{1}{N}\int \mathrm{d}r\,\rho(\mathbf{r})\int \mathrm{d}\mathbf{r}'\rho(\mathbf{r}')[g^{r}(|\mathbf{r} - \mathbf{r}'|, \tilde{\rho}) - 1] = -1 + kT\rho\chi_T \tag{45}$$

where χ_T is the solid isothermal compressibility and ρ its mean density. The above two recipes predict very small values of the effective density and, therefore, are consistent with the above-mentioned intuitive conclusion. By combining any suitable equation of state for the hard-sphere solid phase with any of the two recipes for calculation of the perturbation free energy, the resulting perturbation theory predicts[392,394,395] the solid−liquid transition for several model potentials in satisfactory agreement with the corresponding simulation results.

The simple MFA has been recently extended[396] to a Lennard-Jones solid having a small fraction of vacancies present in the lattice. To this end, the test density function was modified from its usual form to take into account the presence of vacancies and $F_0([\rho])$ was calculated in terms of an equivalent hard sphere system treated by means of a modified WDA[361] (MWDA). It was found that at the liquid-crystal coexistence the vacancy concentration is dependent on temperature.

Perturbation Weighted Density Approximation (PWDA)

Although the WDA[359,361] was originally devised to cope with the inhomogeneous hard-sphere fluid, its physical foundation does not exclude its use to construct functionals for the perturbation term. In practice, the possibility that the weighted density, as an argument of the bulk thermodynamic and/or structural functions, enters the vapor−liquid coexistence region of the phase diagram perhaps does not favor, to some extent, the WDA application in modeling the functional of the perturbation term, but exceptions truly exist. Thus, the WDA has been used[397] to construct a functional for the square well tail term

$$F_{\mathrm{per}}([\rho]) = \int \mathrm{d}\mathbf{r}\,\rho(\mathbf{r})\,f_{\mathrm{per}}(\tilde{\rho}(\mathbf{r})) \tag{46}$$

where f_{per} stands for the bulk excess Helmholtz free energy per particle, corresponding to the perturbation part, and $\tilde{\rho}(\mathbf{r})$ was calculated, as usual, in the form

$$\tilde{\rho}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'\,\rho(\mathbf{r}')\,\omega(|\mathbf{r} - \mathbf{r}'|;\tilde{\rho}(\mathbf{r})) \tag{47}$$

using a normalized negative SW tail as the weighting function[397]

$$\omega(\mathbf{r}) = -\beta u_{\mathrm{a}}(\mathbf{r})/\int \mathrm{d}\mathbf{r}\,(-\beta u_{\mathrm{a}}(\mathbf{r})) \tag{48}$$

In ref 397, eq 46 was combined with a MFA for f_{per} and a version of the WDA for the hard-sphere repulsive contribution. The resulting DFT approach predicts the wetting and drying transitions of the SW fluid at solid surfaces and also compares favorably with the simulation results. A more sophisticated WDA version was proposed[398] for the perturbation term wherein the weighting function is expanded to *n*-th order in density, an approach first used by Tarazona.[399] The required input information is only the bulk second-order DCF at nonzero density points and an equation of state for the fluid under consideration. The $n = 1$ and $n = 2$ versions of this PWDA approach, in combination with the FMF for the hard sphere term, were numerically implemented for both supercritical and subcritical temperatures for the LJ fluid, and it was found that the $n = 1$ version performs more satisfactorily than the plain MFA for supercritical adsorption and the same is true for the $n = 2$ version for the subcritical prewetting transition.[357,361,398]

In contrast with ref 398, wherein the weighting function is a function of a position-dependent weighted density, other authors[400] used a position-independent weighted density $\hat{\rho}$ as an argument of the weighting function to calculate the weighted density $\tilde{\rho}$, i.e.

$$\tilde{\rho}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'\,\rho(\mathbf{r}')\,\omega(|\mathbf{r} - \mathbf{r}'|;\hat{\rho}) \tag{49}$$

where

$$\hat{\rho}[\rho] = 1/N\int \mathrm{d}r\,\mathrm{d}\mathbf{r}'\,\rho(\mathbf{r})\,\rho(\mathbf{r}')\,\omega(|\mathbf{r} - \mathbf{r}'|;\hat{\rho}) \tag{50}$$

and the weighting function is simply given by

$$\omega(\mathbf{r},\rho) = c^{(2)}_{\mathrm{att}}(\mathbf{r};\rho_{\mathrm{b}}) / \int \mathrm{d}\mathbf{r}\, c^{(2)}_{\mathrm{att}}(\mathbf{r};\rho_{\mathrm{b}}) \qquad (51)$$

where $c^{(2)}_{\mathrm{att}}(\mathbf{r};\rho_{\mathrm{b}})$ is the bulk second-order DCF corresponding to the perturbation part and is obtained by removing the bulk hard sphere second-order DCF from the bulk second-order DCF of the fluid of interest. Obviously, besides f_{per}, this version of PWDA needs the bulk second-order DCF of both the considered fluid and hard sphere fluid as input. As a result, this version may break down when applied to subcritical situations. In contrast, it has been shown that the version works well for the LJ fluid supercritical adsorption.

Recently, a carefully designed PWDA has been proposed.[180] It is similar to the procedures adopted in ref 400 but differs in that (i) it employs eq 49 but substitutes $\hat{\rho}$ by a coexistence bulk density ρ_{b}, (ii) it employs eq 46 but the f_{per} comes from a recently proposed fifth-order TPT,[180] (iii) it also employs eq 51 but $c^{(2)}(\mathbf{r};\rho_{\mathrm{b}})$ comes from a proposed analytical expression which is made consistent with f_{per} by means of a scaling procedure using an appropriate factor. Because the acquisition of the analytical expression does not resort to a numerical solution of the OZ integral equation theory, it applies to the entire phase diagram. As a result, this PWDA version works well for both supercritical and subcritical temperature regions.

Partitioned Density Functional Approximation and "Universal" Theoretical Way

A free energy model for inhomogeneous fluid mixtures of charged hard spheres with Yukawa tails was considered in ref 401. The model separates the excess free energy into the hard-sphere (HS) and charge (C) parts. It was considered that a FPE of the charge contribution to the free energy for the inhomogeneous fluid around its uniform limit is, in the strong-coupling limit, practically terminated at second order. In turn, the second-order FPE approximation cannot lead to large errors for weak coupling. Using the WDA concept, it has been proved[402] that the second-order FPE of $c^{(1)}(\mathbf{r},[\rho])$ around the bulk limit is sufficiently reliable in the case of weak dependence of the bulk second-order DCF on its density argument. For a potential function with a highly repulsive core at short distances, the tail part of the bulk second-order DCF is surely very weakly dependent on the density argument, as shown by numerous solutions based on the OZ integral equation theory. As a result, the second-order FPE approximation should be truly highly accurate for the perturbation part. Generalization of the proof to many-component systems is straightforward. Integrating $c^{(1)}(\mathbf{r},[\rho])$ leads to the single component version of the free energy model.[401] Therefore, ref 402 gives actually a proof of the intuitive conclusion of ref 401 and generalizes the conclusion to any potential functions with a highly repulsive core at short distances. If the OZ integral equation is solved under a mean spherical approximation, the resulting bulk second-order DCF is completely density-independent for the perturbation part. According to the proof given in ref 402, the second-order FPE approximation for the perturbation contribution is exact, a point that is obviously appreciated and applied in the literature.[372,373,402,403]

Several DFAs for nonhard sphere fluids have been derived from the above finding. These DFAs divide the potential and correlation functions of interest into a hard core part and a perturbation part and then employ the second-order FPE approximation to cope with the perturbation part, and various hard-sphere DFAs for the hard-core part. Thus, refs 373 and 402 and 403 employ for the hard core part the LTDFA, whereas ref 372 uses the third-order FPE approximation,[375] and all of them consider the second-order FPE approximation for the perturbation part. The resulting DFAs perform well for the density profile calculation of the hard-core attractive Yukawa and Lennard-Jones model fluids. The third-order + second-order perturbation DFT reported in ref 372 subsequently was applied[404] to model fluids with interaction potentials other than the hard-core attractive Yukawa one, and it was found that the DFA is adequately accurate only on the condition that the imported bulk second-order DCF is sufficiently reliable. In particular, it was found[405] that the third-order + second-order perturbation DFT is in the same measure applicable to the hard-sphere + repulsive tail potential function. In ref 352 the inhomogeneous Lennard-Jones fluid was studied by employing the second-order perturbation for the tail part and the FMF for the hard core part; the input, the bulk second-order DCF, is obtained from the first-order MSA.[352] The resulting DFA displays satisfactory performance for predicting density profiles originating from the LJ fluid subjected to several kinds of external field. Another proposed approach, the so-called *"universal" theoretical way*,[406] makes use of the second-order FPE approximation for the tail part, but the hard-core part is substituted by the hard-sphere model with an effective hard-sphere diameter. One key point of the perturbation expansion for the hard-core part is kept unchanged whereas the sum of the expansion terms beyond the leading one is replaced by the corresponding sum for the effective hard-sphere fluid. The final effect is equal to a combination of the second-order FPE approximation for the sum of the hard-core and tail parts and an additional term representing the sum of the terms beyond the leading one and modeled by an effective hard-sphere fluid. It was found that that, in combination with the LTDFA,[381] performs outstandingly well and, in fact, much better than any other existing DFA.

Within the category of the partitioned DFA, we can also include the work of Tang and Wu,[407] who employed the first-order mean-spherical approximation via the energy route for the functional of the intermolecular attractive forces and improved the MFA for the inhomogeneous Lennard-Jones fluid.

IV.3. Perturbation Density Functional Approximation for Inhomogeneous Chain Molecules

The perturbation DFA (PDFA) for inhomogeneous chain molecules was formulated[408] by applying the Wertheim's TPT for polymerization.[78−81] An approximate expression of the intrinsic Helmholtz free energy of a fluid of rigid or flexible molecules was expressed[408] as a functional of the full single molecule distribution function in the limit of complete association in a multicomponent mixture of atoms interacting by forces of chemical bonding type. In the PDFA, the excess contribution to the free energy is calculated perturbatively over a reference fluid of monomers at the same temperature and singlet density as the real system. The PDFA goes beyond self-consistent field theory[409] in that it is the intramolecular distribution function which appears as the central quantity of the PDFA, while the DFT of the type of the self-consistent field (SCF) approximation employs the monomer density as the central variable. Accordingly, the set of coupled Euler−Lagrange equations in the DFT of the type of the SCF approximation can be closed at the level of the monomer density, without resorting to two-point or multipoint functions, as in the TPT1 or TPTN versions of the PDFA, which obviously can be considered as less numerically demanding. The PDFA was found to be appropriate[408,410] for studying nonoverlapping hard-sphere polyatomic fluids in the presence of external fields (such as near a hard wall and in a slitlike pore). The intermolecular structure of the uniform chain fluids also can be obtained[408] in the framework of the PDFA by functional differentiation and inversion of the Ornstein−Zernike equation. As noted by the authors of the PDFA, it is difficult to apply it to overlapping associating monomers. Applications to systems with attractive interactions between associating monomers and/or monomers and surfaces neither have been reported. Compared to the DFT of the type of the SCF approximation for inhomogeneous chain molecules,[409,411] the PDFA is more microscopic and supplies more information about the monomer density distribution. As an approximation surpassing the SCF one, the PDFA supplies a starting point for further simplifications and practical applications, and it should be paid much attention. However, proper attention is not given to the PDFA formalism.[408]

Application of the Wertheim's TPT to inhomogeneous chain fluids also can adopt the form of an interfacial statistical associating fluid theory[412] (iSAFT). The iSAFT expresses the inhomogeneous Helmholtz free energy as the corresponding homogeneous SAFT one evaluated at appropriate weighted densities, except that the inhomogeneous ideal monomer term is obtained by simply replacing the monomer density by the monomer density distribution. Accordingly, more than one kind of weighted densities is needed to convey the inhomogeneous expression. A ruling advantage of the iSAFT may lie in its monomer-based character; this character makes the computational expense of the iSAFT far less demanding than that of the molecule-based polymer PDFA[408] and actually approximately equal to that of the atomic DFT. One kind of the molecule-based polymer DFT[413] also expresses the inhomogeneous free energy due to excluded-volume effects and chain connectivity by using the free energy of the homogeneous fluid evaluated at weighted densities. A basic distinction between the two approaches[412,413] lies in that the molecule-based polymer DFT[413] accounts for the intramolecular interactions due to the direct bonding potential by an ideal free energy functional, which is based on the full single molecule distribution function, while the iSAFT takes account of the free energy contributions due to the direct bonding potential by a so-called association free energy term of the bulk SAFT evaluated at an appropriate weighted density. The many body nature of the molecule distribution function and bonding constraints lead to extremely complicated density profile equations of the molecule-based polymer DFT, whose numerical solution is possible only on condition that the considered polymer is a freely jointed tangent chain.[413,414] For other kinds of polymer molecules, the solution of the density profile equations requires the help of a single polymer chain simulation.[415] It has been found[412] that the iSAFT offers an accuracy comparable to that of the molecule-based polymer DFT, but the computational expense for the iSAFT is largely reduced. It has been indicated[416] that the iSAFT can successfully be applied to study polymer melts, solutions, and blends confined in slitlike pores. One advanced version of the iSAFT suitable for complex fluids of biological interest has also been advanced recently.[417]

There exist other theoretical ways also belonging to the kind of perturbation approach and suitable for tackling inhomogeneous phenomena. Shih, Wang, Zeng, and Stroud presented[418] a generalization of the Ginzburg−Landau formalism to investigate the interfacial tension between simple solids and their coexisting liquids. This simple order-parameter theory uses the amplitude of the density wave at the smallest nonzero reciprocal-lattice vector of the solid as the principal order parameter, and the density difference between solid and liquid is included to second order. Although oversimplified, the approach has the advantage that all the parameters entering the theory can be deduced in a simple fashion from bulk properties, which may then be used to predict surface properties. Particularly, the theory can be used to discriminate between states of different symmetry and behaviors along different crystalline interfaces.

V. Other Advances in Perturbation Theories for Topics of Chemical Interest

Along with the development of the statistical mechanics theory of liquids, some traditional physical chemistry topics, which previously mainly dealt with thermodynamic approaches,[419] are now tackled successfully with microscopic statistical mechanics approaches. In the past two decades, many novel perturbation methods have been developed to handle problems such as solvation phenomena, the origin of hydrophobicity, molecular liquids and complex fluids, nucleation, wetting and drying transitions, capillary condensation, etc. In addition to the above discussion about the progress of the perturbation methods in liquid theories, we will give an overview of applications of the perturbation approaches in molecular liquids and complex fluids, solvation free energy, and hydrophobicity. As for the nucleation phenomenon and phase transitions under confining conditions, such as wetting and dewetting transitions, capillary condensation, and so on, because they currently mainly fall into the field of the DFT, they are beyond the scope of the present review.

V.1. Molecular Liquids and Complex Fluids

Molecular liquids are characterized by orientation-dependent intermolecular potentials made up of a number of site−site interactions of different kinds. Taking water as an example, three main types of interaction between the water molecules can be identified:[420] (i) short-range repulsion, (ii) short-range strongly orientation-dependent attractions (identified as hydrogen bonding), and (iii) long-range electrostatic (primarily dipole−dipole) interactions. Complex intermolecular interactions conduce to anomalous thermodynamic behavior of liquid water, such as a temperature of maximum density in the liquid phase, a negative thermal expansion coefficient in the liquid range, and a large heat capacity. Persuasive explanation and prediction for these anomalies at the molecular level is truly a challenge to traditional theoretical approaches well established for simple liquids with underlying spherically symmetrical potentials.

For the formulation of a perturbation theory, the most important parts are the definition of the reference system, around which the perturbation expansion is implemented, and the rapid and reliable determination of the thermodynamic properties and structure functions of the reference system, preferably in an analytical form. To ensure convergence of the perturbation expansion, it is requested that the structure and thermodynamic properties of the realistic fluids are determined mainly by those of the chosen reference system. Computer simulations reveal[421] that the structures of the real water and its short-range (both repulsive and attractive) counterpart are nearly identical regardless of the thermodynamic conditions considered. A short-range reference system has been defined[422] in such a way that the perturbation expansion is written in powers of the dipole–dipole interaction only. It was shown that this reference system provides the same structure and thermodynamics as other reference systems used in ref 421 and captures, for three realistic model potentials of water (two nonpolarizable ST2 and TIP4P models and one polarizable TIP4P/P model), at least 95% of the total internal energy over the entire temperature-density plane. An analytic expression for the Helmholtz free energy of a short-range reference system obtained from the TIP4P model potential of water has been derived recently[423] by deducting the long-range part of the Coulombic interactions. In agreement with previous conclusions, it was found[423] that the short-range reference system exhibits, in addition to a faithful representation of the structure of water, the same anomalous features that are characteristic for real water. All of these findings indicate that the perturbation approach is qualified to become a justified tool to be used to develop a molecular theory for water. Wertheim's thermodynamic perturbation theory for associating fluids was applied[424] to a two-dimensional model of water, and it was found that the resulting TPT approach gives quantitative agreement with the MC simulations for "hot" liquid water, although it does not predict the properties of "cold" water equally well. By replacing the hard-disk reference system of ref 424 by a Lennard-Jones reference system and calculating the effective density of the reference system self-consistently, a revised TPT for the same model of water has been proposed recently,[425] showing a significant improvement over the original version in that it predicts the key anomalies of "cold" water, such as a minimum in the molar volume and large heat capacity.

Apart from various modifications of the SAFT approach, the application of the perturbation approach to complex fluids is mainly based on the phenomenological GL theory.

A modified single order parameter GL free energy, which yields several modulated phases and their coexistences, is given[426] by

$$F\{\phi(\mathbf{r})\} = \int \mathrm{d}\mathbf{r}\left[2(\nabla^2\phi)^2 - 2(\nabla\phi)^2 + \frac{\tau}{2}\phi^2 + \frac{1}{4}\phi^4\right] \tag{52}$$

where $\phi(\mathbf{r}) = \psi(\mathbf{r}) - \psi_c$ is the order parameter, in which ψ_c is the composition at the critical temperature T_c, and $\tau = (T - T_c)/T_c$ is the reduced temperature. The spatial modulations are preferred due to the negative coefficient of the gradient square term and the competition between this term and the Laplacian square term. Such a free energy functional has been used to describe various systems such as diblock copolymers,[427] Langmuir films,[428] magnetic layers,[429] and microemulsions[430] and to calculate for diblock copolymer morphologies[431] and the relative stability of the lamellar and hexagonal phase.[432] The dynamical extension of the free energy functional is employed to describe the dynamics of the lamellar–hexagonal phase separation,[433] pattern formation and nucleated growth in a binary phase-separating liquid,[434] and the phase separation process[435] of a two component miscible system that demixes due to the inclusion of a third component that interacts preferentially with one of the two components.

Controlling the morphology of the domains generated by the phase separations helps to design and regulate physical properties of the polymer materials such as permeability, electrical conductivity, and mechanical properties. One kind of phenomenological DFT based on the time-dependent GL scheme has been being used to investigate the mechanism of the phase separation and the domain formation of polymer materials. To obtain theoretically the phase diagram of a diblock copolymer, Leibler[436] employs a power series expansion of the free energy up to the fourth-order terms in the segment density fluctuations wherein the expansion coefficients are evaluated using the random phase approximation (RPA). Ohta and Kawasaki[437] used a simpler form of the Leibler expansion and a long-range part while the long-range part is approximated by the long-range asymptotic form of the second-order term in the expansion; the OK theory succeeds in qualitatively reproducing the phase diagram of the microdomain structures of the diblock copolymer in the strong segregation region. Bohbot-Raviv and Wang[438] evaluated the second-order term using the RPA and combined it with the higher order terms in the expansion of the Flory–Huggins free energy; this theory predicted several microdomain structures of star polymers and linear triblock copolymers. Uneyama and Doi[439] generalized the OK theory to melts and blends of any types of polymer architectures, i.e., the branching structure and the order of the sequence of the segments along the chain, and reproduced micellar structures, obtaining a phase behavior of the micelles that is in agreement with the experimental phase diagram. Due to the truncation error of the Taylor expansion of the free energy used in the phenomenological DFT, and the sizable effect of the truncation error from the intermediate to the strong segregation regions, these phenomenological DFT approaches break down in the strong segregation region. A hybrid dynamic DFT[440] has been developed from a combination of the dynamic self-consistent field (SCF) theory and a time-dependent GL type theory. The hybrid theory makes use of both the accuracy of the SCF theory in both weak and strong segregation regions and the advantage of the modest amount of computational cost required by the phenomenological DFT, and it reproduces the metastable complex phase-separated domain structures of an ABC triblock copolymer observed by experiments.

In ref 441 it is shown that the Landau model provides a general framework for studying glassy dynamics in a variety of systems, such as supercooled liquids, foams, and granular matter. In combination with the nanothermodynamics, the Landau theory for phase transitions has been adapted[442] to treat finite-sized thermal fluctuations inside bulk complex fluids; the resulting theory yields a Vogel–Fulcher–Tammann-type relaxation rate, typical of a glass transition, and provides an explanation for the distribution of relaxation times and heterogeneity that are found in glass-forming liquids. The time-dependent GL equation[443] also successfully describes the phenomenon of critical slowing down, whereby the relaxation time for the order parameter fluctuations scales as a power of the correlation length, which in turn diverges as the critical point is approached. In ref 444 a Ginzburg–Landau type equation is proposed and used to explain the Fischer cluster phenomenon, the so-called long-range correlations of density fluctuations, for glass-forming liquids.

V.2. Solvation Free Energy and Hydrophobicity

Solvation free energy (hydration free energy in water or aqueous solutions), a crucial quantity in understanding the degree of solubility of solute in solvents, is defined as the free energy of transfer from a vacuum (or infinitely dilute gas) to a solvent. Since the solvation free energy strongly depends on the solvent density and composition and can much exceed kT, it is a basic and essential quantity for calculating solubilities, partition coefficients, binding affinities in host−guest systems, etc. and plays various important roles in many processes, such as formation of micelles and biological membranes, protein folding, enzyme catalysis, molecular recognition among proteins, and aggregation of transmembrane helices, drug delivery to receptors, and so on. The enumerated examples have been the main subjects in soft matter physics.

Perturbation strategy tackling solvation phenomena can roughly be classified into five kinds. One is the thermodynamic perturbation theory (TPT); another is the perturbation density functional theory (PDFT) approach; another is a computer simulation technique based on free energy perturbation; finally, one has the Ginzburg−Landau type approach and the distribution function integral equation approach. We will illustrate these five kinds of perturbation approaches with representative examples.

Thermodynamic Perturbation Theory

A Padé truncation approximation of the TPT due to Stell and co-workers[445] has been used to calculate the solvation chemical potential of a dipolar solute in a model fluid of dipolar hard spheres. It was shown[446] that the basic failure of continuum theories consists in their inaccurate description of the internal energy and entropy of solvation. However, the Padé truncation approximation calculates the solvation chemical potential, in agreement with the whole body of simulation results, within an accuracy of 3%; the internal energy and entropy of solvation are also accurately described by the Padé truncation approximation. One of the merits of the Padé truncation approximation is its analytical simplicity and ease of including the molecular (generally anisotropic) polarizability. A semiempirical approach for predicting the work of formation of a cavity inside a model fluid, specifically for fluids that contain an attractive term in the intermolecular potential, has been proposed[447] by combining the scaled particle theory for hard particle fluids and the free energy perturbation method for the perturbation term. Following the procedure used in bulk TPT, the work of formation of a cavity is decomposed in ref 447 into a reference part and a perturbation part. By mapping the reference system to a hard sphere fluid with an appropriate effective density, the former can be calculated by using an expression for the work of cavity formation within a hard-sphere fluid obtained by Matyushov and Ladanyi,[448] while the perturbation part is calculated in a mean field manner analogous to that for the bulk fluid, by neglecting the correlations inside the fluid due to the presence of the cavity except for the fact that the local solvent density inside the cavity is set to zero as it is. This approach appears to be valid over a broad range of conditions, even performing well when the fluid is metastable. A TPT for hydrophobic hydration has been constructed[449] based on an analytical cavity formation equation of state. The TPT approach was found[449] to compare favorably with experimental rare-gas solubility data; it predicts a strong temperature dependence of the critical length scale for the hydrophobic dewetting transition and can evaluate the fundamental solute−solvent interaction contributions to rare-gas hydration chemical potentials. As the cavity equation of state is built on pure water experimental and simulation data, it accurately spans the atomic, molecular, mesoscopic, and macroscopic cavity size regimes over a wider region of the water phase diagram. Particularly, this allows the TPT approach to be extended realistically to regimes in which direct measurements are not available. In ref 450, the TPT was applied to study the transfer of two-dimensional Lennard-Jones solutes into the two-dimensional Lennard-Jones solvent and the necessary expressions to calculate the transfer properties were derived. It was found[450] that the TPT results agreed very accurately with the exact computer simulation data, which provides some confidence in the application of the TPT to more realistic systems. It should be pointed out that the 2D Lennard-Jones fluid can be used as a reference system of the two-dimensional MB model of water, as this model, when stripped off the hydrogen bonding arms, is just a 2D Lennard-Jones fluid.[424,451]

Perturbation Density Functional Theory

Perturbation DFT was used to investigate the hydration forces between two infinite planar surfaces in ref 452, where it is found that the most important feature of the surface−solvent potential that governs primarily the solvation force is its range, whereas the effect of using an orienting surface−solvent potential is of secondary importance. In ref 453 was addressed at length the dependence of the properties of the solvation force between identical planar walls on the wall−fluid potential and the thermodynamic state of an intervening solvent with a truncated LJ potential. It was found[453] that, for long-ranged wall−fluid potentials decaying as $-Az^{-p}$, $z \to \infty$, with various values of p, the solvation force is always repulsive away from the critical region of the bulk LJ fluid. For large wall separations L, the solvation force can be decomposed into a positive regular part and a negative singular part; in particular, the regular part decays with the same power law as the wall−fluid potential, and the singular part is responsible for the critical singularities at the bulk critical point and vanishingly small away from the critical region. Perturbation DFT has also been used recently to explore the solvation properties and the local solvent density augmentation of a spherical solute immersed in a monatomic fluid and a supercritical diatomic fluid, respectively.[454] It has been found that the behavior of the local coordination number in homonuclear diatomic fluids follows trends similar to those reported in previous studies for monatomic fluids; the associated solvation free energies exhibit a nonmonotonous behavior as a function of density for systems with weak solute−solvent interactions, and the solute−solvent interaction anisotropies have a major influence on the nature and extent of local solvent density inhomogeneities and on the value of the solvation free energies in supercritical solutions of heteronuclear molecules. On the basis of the perturbation DFT approach, a theory for solvophobic phenomena which can predict the spacial packing behavior of solvent as well as the free energy of solvation and the free energy cost of solvating cavities has been developed by Sun.[455] The most remarkable characteristic of this perturbation DFT approach lies in that it does not have to rely on a particular potential function of the solvent−solvent interaction. Rather, it is based on experimentally observed liquid structure and thermodynamic observables such as equation of state and surface tension. As a result, the approach is able to treat molecular liquids in a fashion very similar to simple fluids with an underlying spherically symmetrical potential function. The author employs the approach to investigate the cavity formation in liquid water, and encouragingly, the theoretically calculated excess chemical potential and cavity−water radial distribution function are in very satisfactory agreement with experimentally measured values and computer simulation results based on a SPC model of water. Another recent application of the perturbation DFT formalism is the solvation in a molecular solvent,[456] taking into account the microscopic structure of the solvent, the dipolar saturation, and the nonlocal character of the dielectric constant. It was shown[456] that the functional can be minimized numerically on a three-dimensional grid around a solute of complex shape to provide, in a single shot, both the solvent local density and the absolute solvation free energy. Many relative quantities, such as association constants or affinities, can be deduced from the absolute solvation free energy. The main inadequacies of this recipe are that (i) the functional is actually a lowest functional perturbation expansion approximation, and an additional approximation is needed to calculate the free energy from the solvent local density; and that (ii) important features of water, such as a H-bonding network-induced tetrahedral symmetry, are still lacking in the functional. It was noted that the functional can be reduced to the conventional implicit solvent model after some macroscopic simplifications are made.

Computer Simulation-Free Energy Perturbation

The most rigorous and reliable approach for estimation of the solvation free energy using molecular dynamics or Monte Carlo simulations is the free energy perturbation (FEP),[457] which was thoroughly refined during the 1990s to allow for systematic estimation of the absolute free energies of solvation in combination with appropriate thermodynamic cycles. The computer simulation−FEP methodology can be divided into two subtypes, the so-called stepwise FEP and the one-step FEP; both types are based on application of the thermodynamic perturbation formula of Zwanzig[1]

$$\Delta G_{\mathrm{BA}} \equiv G_{\mathrm{B}} - G_{\mathrm{A}} = -RT \ln\langle e^{-(H^{\mathrm{B}}-H^{\mathrm{A}})/RT}\rangle_{\mathrm{A}} \tag{53}$$

which allows the free energy of an end-state B to be determined from the free energy and an ensemble of a reference state A. Here *R* is the molar gas constant, *V* is the volume of the system, and $\langle\ \rangle$ denotes an ensemble average. By a careful choice of the reference state A, the absolute free energy for a number of different end-states (B, C, D,...) can be predicted from a single simulation, given that the free energy of the reference state A is known. In the stepwise FEP, the computation of ΔG_{BA} in the isothermal−isobaric constant *NpT* ensemble is split into N' intermediate contiguous states defined by the coupling constant λ; as λ goes from 0 to 1, the classical Hamiltonian $H(\mathbf{r}^N)$ varies from $H^{\mathrm{A}}(\mathbf{r}^N)$ to $H^{\mathrm{B}}(\mathbf{r}^N)$. The total ΔG_{BA} is then a sum of the Gibbs free energy differences between a series of closely related intermediate states defined by λ.

$$\Delta G_{\mathrm{BA}} \equiv G_{\mathrm{B}} - G_{\mathrm{A}} = \sum_{i=1}^{N'} \Delta G(\lambda_i)$$

$$= \sum_{\lambda=0}^{1} - RT \ln\left\langle \frac{V e^{-(H(\mathrm{r}^N;\lambda\pm\Delta\lambda)-H(\mathrm{r}^N;\lambda))/RT}}{\langle V\rangle}\right\rangle_{\lambda} \tag{54}$$

In eq 54 the perturbations are performed in both directions; the difference between forward ($+\ \lambda\delta$) and backward ($-\lambda\delta$) simulations gives a lower-bound estimate of the error in the calculation.[458]

The traditional stepwise FEP can yield an accurate solvation free energy for arbitrary species; representative works are as follows: ref 459 used the MC simulation-orientated FEP method to investigate the effects of solute concentration on the calculated free energy of hydration in a TIP4P water; no remarkable dependence on the solute concentration was found for the electrostatic free energy of hydration. As a result, the technically simpler estimation of the total standard solvation free energy based on simulation for infinitely dilute solutions is acceptable. In ref 458, the FEP method was employed to investigate mutation of complexed $\mathrm{Me_4N^+}$ into complexed $\mathrm{MeNH_3{}^+}$; good agreement was obtained between the computed and experimental relative values of the Gibbs free energy of complexation within a maximal deviation of 13%; by decoupling the different mutations from the initial stage to the final state into several stages, the relative importance of different contributions to the total change in the Gibbs free energy of complexation was shown. Calculation of the enthalpy and entropy change is essential for a better identification of the type of interactions controlling the association process; operational expressions for the enthalpy and entropy of association in the *NpT* ensemble with the FEP method were established in ref 460.

The minimal requirement for the one-step FEP is that the reference state Hamiltonian does not have any singularities that are not shared by all of the end-state Hamiltonians. Liu et al.[461,462] demonstrated that the singularities associated with typical molecular mechanics force fields can be removed by constructing “soft” reference states that can be used for efficient one-step FEP. With this procedure, the relative binding free energies for many ligands at a time in proteins such as the T4 lysozyme[462] and the estrogen receptor ligand binding domain[463] were successfully calculated by the one-step FEP. Schäfer et al.[464] showed that a simulation of a single neutral “soft” reference state could be used to accurately (errors <3 kJ/mol) predict the solvation free energies of a range of nonpolar solutes in water. In ref 465 was investigated in detail the choice of reference state for the one-step FEP; it was found that both a neutral reference state and a “soft dipole” reference state based on a charge group scaling of the solute−solvent electrostatic interaction can be appropriate reference states to be used in the one-step FEP method for computation of the solvation free energy of polar solutes. In ref 466, the one-step FEP was applied to a realistic model of the binding of a set of rather large ligands to the protein factor Xa. Three limitations to the choice of the unphysical reference states, which influence the accuracy of the one-step FEP, were identified: size, its flexibility, and its electrostatic character.

In order to obtain the free energy differences for multiple end states from a single simulation by the one-step FEP, it is useful to expand the sampled ensemble. The expanding strategies vary both in theoretical basis and in implementation of the sampling protocol,[465−467] and the most recent development is reported in ref 468.

It should be noted that although eq 53 is formally exact for all choices of states A and B, the convergence of the free energy difference is strongly dependent on the overlap relation of the phase space densities of states A and B.[469] Application of the FEP to more complex problems, such as estimating protein−ligand binding free energies, has been shown to be difficult due to convergence and sampling problems.[470]

Some novel FEP methods are summarized next. The ab initio/classical FEP method was introduced in ref 471 and subsequently tested on a solute in water.[472] It was shown[473] that the method is applicable to ion solvation in water and can predict the well-known values for the free energies of hydration of Na^+ and Cl^- at 573 K and 0.725 g/cm^3 within 4 kJ/mol. It was also shown[474] that the ab initio/classical FEP method can provide a practical and systematic means of developing new model potentials, validating their predictions, and correcting their errors. The advantages of the ab initio/classical FEP method over the computer simulation-orientated FEP method and ab initio MD simulation lie in the fact that the accuracy of the ab initio/classical FEP method is not limited by the accuracy of the approximate potentials used and it is only necessary to determine ab initio energies at a small number of configurations, taken from the simulation with the approximate model. A novel FEP method has been proposed[475] to compute the free energy of transferring a molecule between fluid phases, which consists in drawing a free-energy profile of the target molecule moving across a binary-phase structure built in the computer. The novelty of the method lies in the point that the definition of the free energy profile is distinct from the common definition. Like the traditional FEP method, the method in ref 475 is also equally applicable within the MD and MC frameworks, independently of the way of generating statistical ensembles. The method is used to evaluate the gas solubility and vapor pressure of several organic molecules, and the calculated results are generally in good agreement with experiments. Besides the vapor−liquid equilibrium, the liquid−liquid equilibrium of mixtures is clearly also a possible application of the method.

Ginzburg−Landau Type Approach

Quite recently, Onuki presented[476] a Ginzburg−Landau type theory for solvation of ions in polar binary mixtures. This scheme accounts for electrostatics with an inhomogeneous dielectric constant, solvation effects, and image forces. With this Ginzburg−Landau scheme, the ion-induced nucleation in a gas phase of polar one-component fluids was investigated; it was shown[477] that the solvation free energy is larger in the gas phase than in the liquid phase at the same temperature on the coexistence curve, and this difference reduces greatly the nucleation barrier in a metastable gas phase. The Ginzburg−Landau scheme was employed to study[478] the effects of ions in mixtures of both strong and weak polar fluids by taking account of electrostatic, solvation, and image interactions, and a general expression was derived for the surface tension of electrolyte systems. The solvation effects of charged particles in liquid crystals,[479] and solvation effects in near-critical polar binary mixtures,[480] were also examined with this Ginzburg−Landau scheme.

Distribution Function Integral Equation Theory Approach

The excess chemical potential of solvation can also be obtained from the distribution function integral equation theory by the standard procedure of gradually "switching on" the solute−solvent interactions. When the HNC approximation is used to close the integral equation, the solvation chemical potential is given by a closed analytical expression. However, the solvation chemical potential is no longer analytical if a nonzero bridge function is used for the integral equation. Consequently, one has to solve numerically the integral equation repeatedly at every step of integration over the "switching" parameter; this implies a significant computational effort. By making a functional expansion of the solvation chemical potential around the HNC solution, Kovalenko and Hirata[481] succeed in avoiding repeated numerical solution of the integral equation to obtain the hydration free energy of hydrophobic solutes.

It was noted[482] that Wertheim's theory for associating fluids can be applied to a "Mercedes−Benz" (MB) model of water through the multidensity OZ integral equation theory; this approach explicitly accounts for the coupled orientation dependence of interactions that arises from multiple hydrogen bonding arms within water molecules, and hence, it is qualified to study orientations of water molecules around solutes and not only the distance-dependent structures. The angle-dependent Wertheim OZ integral equation theory is employed[483] to study the hydrophobic effect and transfer of a nonpolar solute into the MB water, and it is shown to reproduce the Monte Carlo results qualitatively for cold water and quantitatively for hot water.

VI. Summary and Outlook

In the preceding sections we have given an overview of the foundations and applications of different perturbative approaches for obtaining the thermodynamic and structural properties of fluids and solids, with emphasis on the most recent developments. Perturbation approaches, on the whole, constitute today the most fruitful procedures to deal with these properties for a huge variety of systems, from simple to complex. In many-body problems such as liquids, analytical solutions rarely exist; we achieve analytical or semianalytical or parametrization solutions only in very few situations. The perturbation approach provides a starting point to tackle complicated many-body problems from these known solutions. In fact, the perturbation approach may be the most easily kept in memory method when one is faced with any new complicated problems. As a result, in the field of liquid theory, perturbation approaches play an important role not only in the traditional field of thermodynamic perturbation theory but also in OZ integral equation theory, in density functional theory, in computer simulation, etc. The perturbation expansion can adopt different forms: it can take the form of an inverse temperature expansion such as HTSE, a coupling parameter expansion such as the numerical Ornstein−Zernike equation perturbation theory, a density expansion such as the virial expansion, a general order parameter expansion such as the Ginzburg−Landau theory, etc. As the perturbation approach only provides, in some cases, a rudimentary treatment, its improvement is necessary by combining it with other theoretical approaches, such as computer simulation, OZ integral equation theory, renormalization group theory, etc., as reviewed in the text. This is the reason why we include in the review theoretical approaches other than thermodynamic perturbation theory, even if any of the above approaches will deserve a single and specific review. In any case, the more effort invested in the research on complex fluids, molecular liquids, and even more complicated biologically interesting systems, the greater will be the role played by perturbation approaches. Correspondingly, an irreversible tendency will be a joint action of the perturbation approach with various other theoretical ways to improve the accuracy.

The flexibility of these theories, the relative simplicity of their application in many cases, their ability for parametrizing experimental data, and the interchangeability of their findings (that is the fact that the outcome from some theories can be used as input for other theories giving rise to hybrid theories, as shown in this short review) will ensure for these approaches a long life cycle and a rapid growth in their usefulness and practical applications in the coming years, as occurred in the last few decades. Unfortunately, this rapid growth will make it in the future very difficult to provide a global overview on these approaches in a single review, as attempted in the present one, as any of the above sections will deserve a specific review, with the drawback that this might obscure the interplay between theories belonging to different approaches. We hope that this review will act as a guide in this field, helping new developments to be placed in due context.

VII. List of Symbols

$f(r)$	Mayer *f*-function
A	Helmholtz free energy (also denoted *F*)
A^{ideal}	ideal gas contribution to the Helmholtz free energy
A^{mono}	monomer contribution to the Helmholtz free energy
A^{chain}	chain contribution to the Helmholtz free energy
A^{assoc}	contribution to the Helmholtz free energy from association
B_n	virial coefficient of order *n*
$B(r)$	bridge function
$c(r)$	direct correlation function
$c^{(1)}(\mathbf{r}[\rho])$	nonuniform first-order direct correlation function
$c_0^{(n)}$	bulk *n*-th direct correlation function
$c_{\mathrm{att}}^{(2)}(\mathbf{r};\rho_b)$	bulk second-order direct correlation function corresponding to the perturbation part of the potential
d	effective diameter
f	Helmholtz free energy per particle
F	Helmholtz free energy (also denoted *A*)
F_n	perturbative contribution of order *n* to the free energy
F_{ex}	excess Helmholtz free energy
F_{per}	perturbation contribution to the excess Helmholtz free energy
$g(r)$	radial distribution function
$g_0(r)$	radial distribution function of the reference system
$g_1(r)$	first-order perturbative contribution to the radial distribution function
$g_{ij}(r)$	partial radial distribution function for particles of species *i* and *j* in a mixture
$g_{ij}^0(r)$	partial radial distribution function for particles of species *i* and *j* in a reference mixture
G	Gibbs free energy
$h(r)$	total correlation function
$H(x)$	Heaviside step function
k	Boltzmann's constant
N	number of particles in the system
N_i	number of intermolecular distances in the range (r_i,r_{i+1})
p	pressure
r	intermolecular distance
r^*	r/σ: reduced distance
T	temperature
T^*	reduced temperature
$u(r)$	intermolecular potential
$u_0(r)$	reference part of the intermolecular potential
$u_1(r)$	perturbation part of the intermolecular potential
$u_1^*(r)$	perturbation part of the intermolecular potential in reduced units
V	volume
$w(r)$	weighting function
x_i	mole fraction of species *i* in a mixture
$y(r)$	cavity function
Z	pV/NkT: compressibility factor

Greek Symbols

β	$1/kT$
δ_{ij}	effective distance of closest approach between the centers of two molecules of species *i* and *j* in a mixture
ε	energy parameter of the potential
λ	coupling parameter and also the width of the square-well potential in reduced units
μ	chemical potential
ρ	N/V: number density
ρ^*	$\sigma\rho^3$: reduced density
$\tilde{\rho}$	effective density
$\hat{\rho}$	weighted density
$\bar{\rho}$	local density averaged over a sphere of appropriate radius
ρ_{b}	bulk density
$\rho(\mathbf{r})$	local density at position $\mathbf{r}$
Φ_1	contribution of the perturbation to the configurational energy of the system
σ	diameter of the hard spheres
σ_{ij}	distance of closest approach between the centers of two spheres of species *i* and *j* in a hard-sphere mixture
μ	chemical potential
χ_T	isothermal compressibility

Abbreviations

BDFA	bridge density functional approximation
BH	Barker−Henderson
BMCSL	Boublík−Mansoori−Carnahan−Starling−Leland
CPE	coupling parameter expansion
DCF	direct correlation function
DFA	density functional approximation
DFT	density functional theory
EOS	equation of state
EXP	exponential approximation
FEP	free energy perturbation
FMF	fundamental measure functional
FMT	fundamental measure theory
FPE	functional perturbation expansion
GL	Ginnzburg−Landau
HB	hard-body
HCY	hard-core Yukawa
HNC	hypernetted-chain theory
HRT	hierarchical reference theory
HS	hard spheres
HTSE	high temperature series expansion
IE	integral equation
LCA	local compressibility approximation
LJ	Lennard-Jones
LTDFA	Lagrangian theorem-based density functional approximation
MB	Mercedes Benz
MC	Monte Carlo

MCA	macroscopic compressibility approximation
MD	molecular dynamics
MFA	mean field approximation
MSA	mean spherical approximation
OCT	optimized cluster theory
ORPA	optimized random phase approximation
PWDA	perturbation weighted density approximation
OK	Ohta−Kawasaki
OZ	Ornstein−Zernike
rdf	radial distribution function
RG	renormalization group
RHNC	reference hypernetted-chain theory
RPA	random phase approximation
SAFT	statistical associating fluid theory
SAFT-HS	original SAFT for molecules consisting in hard-sphere segments
SAFT-VR	variable range SAFT
HR-SAFT, soft-SAFT, DAFT-D,...	different versions of the SAFT
SCOZA	self-consistent Ornstein−Zernike approximation
SS	square shoulder
SW	square well
TPT	thermodynamic perturbation theory
TPTD	dimer version of the TPT
TW	triangle well
VLE	vapor−liquid equilibrium
vdW	van der Waals
vdW1	van der Waals one-fluid theory
WCA	Weeks−Chandler−Andersen
WDA	weighted density approximation

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(285) There are several misprints in Tables 2 and 5 of ref 239. In Table 2, the coeficients corresponding to $n = 6$ and $m = 1$, for $k = 1$, instead of $5\pi^5/7776$ must be $5\pi^5/15552$; for $k = 2$, instead of $2b_0^{(6)}-(5\pi/12)b_0^{(5)} + 11\pi^5/15552$ must be $2b_0^{(6)}-(5\pi/12)b_0^{(5)} + \pi^5/2592$; and for $k = {}^3/_2$, instead of$-b_0^{(6)} + (5\pi/18)b_0^{(5)}- \pi^5/729$ must be$-b_0^{(6)} + (5\pi/18)b_0^{(5)}-17\pi^5/23328$. The coeficients corresponding to $n = 6$ and $m = 5$, for $k = 1$, instead of $2b_0^{(6)}-(5\pi/12)b_0^{(5)} + 11\pi^5/15552$ must be $2b_0^{(6)}-(5\pi/12)b_0^{(5)} + \pi^5/2592$; for $k = 2$, instead of $5\pi^5/7776$ must be $5\pi^5/15552$; for $k = {}^3/_2$, instead of$- b_0^{(6)} + (5\pi/18)b_0^{(5)}-\pi^5/729$ must be$- b_0^{(6)} + (5\pi/18)b_0^{(5)}-17\pi^5/23328$. In Table 5, in the second row of numbers, instead of the first number, 0.286132×10^{-1} must be 0.240132×10^{-1}; instead of the last number, 0.980659×10^{-12} must be 0.976059×10^{-12}.
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