

Thermostatistical description of gas mixtures from space partitionsR. D. Rohrmann^{1,*} and J. Zorec^{2,†}¹*Observatorio, Universidad Nacional de Córdoba, Laprida 854, X5000BGR Córdoba, Argentina*²*Institut d'Astrophysique of Paris, UMR 7095 CNRS, Université Pierre and Marie Curie, 98bis Boulevard Arago, 75014 Paris, France*

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The new mathematical framework based on the free energy of pure classical fluids presented by Rohrmann [Physica A **347**, 221 (2005)] is extended to multicomponent systems to determine thermodynamic and structural properties of chemically complex fluids. Presently, the theory focuses on D -dimensional mixtures in the low-density limit (packing factor $\eta < 0.01$). The formalism combines the free-energy minimization technique with space partitions that assign an available volume v to each particle. v is related to the closeness of the nearest neighbor and provides a useful tool to evaluate the perturbations experimented by particles in a fluid. The theory shows a close relationship between statistical geometry and statistical mechanics. New, unconventional thermodynamic variables and mathematical identities are derived as a result of the space division. Thermodynamic potentials μ_{il} , conjugate variable of the populations N_{il} of particles class i with the nearest neighbors of class l are defined and their relationships with the usual chemical potentials μ_i are established. Systems of hard spheres are treated as illustrative examples and their thermodynamics functions are derived analytically. The low-density expressions obtained agree nicely with those of scaled-particle theory and Percus-Yevick approximation. Several pair distribution functions are introduced and evaluated. Analytical expressions are also presented for hard spheres with attractive forces due to Kac-tails and square-well potentials. Finally, we derive general chemical equilibrium conditions.

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I. INTRODUCTION

The detailed knowledge of atomic and molecular populations is essential to analyze and evaluate accurately thermodynamic properties and chemical processes in fluids as well as their monochromatic opacities. In particular, they are required in studies of stellar interiors, atmospheres and circumstellar envelopes. Gas densities in stellar atmospheres and circumstellar structures are low, they are hardly higher than 0.001 g cm^{-3} . Nevertheless, in these cases it is necessary to deal with a high variety of particles and electronic configurations and therefore, with a series of physical processes to calculate the radiation emitted by the star accurately [1,2].

Among the most difficult challenges in determining gas models is to obtain self-consistently atomic densities and opacity absorption coefficients by taking into account the nonideal effects. The source of nonideal effects is the presence of Coulombic interactions between charged particles as well as due to the short-ranged interactions between neutral-neutral and neutral-charged particles. Due to its relevance and complexity, the elaboration of gas models from mechanical statistical approaches is still an active area of research today [3–12].

The present study is motivated by the difficulties of predicting quantitatively the optical properties of stellar atmospheres. In typical gas models the opacity data are obtained through a complimentary calculation once the equations of state and mean abundances of bound states are obtained. This procedure can produce, however, internal inconsistencies in a model, mainly when the abundances of atoms are calculated

using internal energies that are different from those assumed to obtain the radiative transitions [13,14]. This can lead to serious disagreements between predictions and observations or experiments (e.g., the unphysical Lyman opacity [15]). Therefore, it is highly desirable to develop a theoretical formalism that treats atoms subjected to different perturbations by considering them in separate groups and evaluate accordingly the populations and opacities in a consistent way. Such a gas model must then consider explicitly not only all atomic excited states but also do they need to discriminate different perturbation states with the use of an appropriate particle-state variable. Our work is then oriented to develop a model with these characteristics.

With the aim of establishing a detailed and accurate equation of state for fluids, in a previous work we have developed a gas statistical formalism which combines free energy minimization methods with space partitions [13]. The feature of this formalism, as compared to other more standard and well-established statistical-mechanical theories of the fluid-liquid state, is the attempt of keeping trace, in a thermodynamically self-consistent way, of a more refined structural information on the local environment of a given particle through an extra parameter, the “available volume,” which is determined by the distance of the reference particle to its closest neighbor. For noninteracting particles, the available volume “ v ” is equivalent to the spherical volume whose radius is the distance between the respective centers of the particle and its nearest neighbor. This volume is considerably smaller for particles with repulsive interactions. The theory [13] was formulated for one-component dilute fluids, where the Helmholtz free energy is written in terms of the occupation number distribution N_v of the v variable and where the particle interactions are introduced using pair potentials. The result thus obtained represents a unified treatment of thermodynamics and the structure of fluids. The formulation was

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applied to hydrogen atoms in an electrically neutral medium of charged particles encompassing ions and electrons. The atomic populations were derived by establishing groups of atoms having different plasma perturbations measured according to the size of their available space volumes v . Although the results obtained are only illustrative of its possible performances, this theory represents the first attempt of evaluating in detail the populations by combining consistently the plasma interaction effects.

Approaches based on space partitions were attempted in the past with the so-called “cell” theories to obtain equations of state for fluids. However, the character of these space divisions is quite different as compared to that employed in Ref. [13] and in the present paper. The cell models [16–18] were originally developed by Eyring and Hirschfelder [19] and by Lennard-Jones and Devonshire [20]. They were inspired by the latticelike configurations acquired by some systems at high densities. In such theories the fluid volume is divided into an imaginary lattice of cells. Each particle is then confined into a cell, which implies that a space partition is assumed beforehand, instead of being deduced from the model proper. Besides, by ignoring the interchange of particles between cells, an error is introduced in the system-entropy calculation, which is usually corrected using an arbitrary “communal entropy” factor.

The perspective of the theory presented in Ref. [13] is new, as it determines a space division by assigning the v volume to the particles. This is achieved by minimizing the system free energy under the condition that the sum of all v volumes be equivalent to the entire volume of the fluid. In this procedure, no particle confinement is established, because the assignment of an individual volume to each particle does not introduce any ownership connection between space regions and particles, i.e., v does not carry any information on the particle coordinates. Therefore, the formulation presented in Ref. [13] is free from difficulties that are inherent to the cell theories, i.e., entropy corrections, and it can provide new results, such as the combined thermodynamical and structural information of a fluid, which cannot be derived from the cell models.

In the present paper we generalize the formalism to D -dimensional multicomponent fluids that was initially developed in Ref. [13] only for pure or single-component substances. It aims at giving particularly simple analytic forms to provide a unified derivation of thermodynamic and geometric properties that characterize them. The formulation of the theory is general, but attention is focused on its application to hard sphere models, which represent the repulsive interactions among atoms and geometrically simple molecules [21]. We also include the analysis of hard spheres with weak long-range attraction (Kac type) and hard spheres with square-well potential. The approximations discussed here should be suitable for more realistic short-ranged potentials, like those governing many atomic and colloidal fluids. Our introduction of space partitions in statistical thermodynamics marks a considerable progress in the description of gases with respect to previous theories, since it gives the possibility of obtaining thermodynamic and structural information on fluids simultaneously and self-consistently. The present extension to multicomponent fluids enables us to treat arbi-

trarily complex chemical mixtures by including systematically the interparticle interaction potentials. The theory can have many applications, not only in astrophysics, but also in other fields such as the analysis of colloidal and protein solutions in biochemistry.

In the following sections, we first introduce a description of states of a gas mixture based on space partitions. General expressions for the Helmholtz free energy are presented in Sec. III and the thermodynamic equilibrium states are derived in Sec. IV. We analyze there some nonconventional thermodynamic variables that are generated by the theory and derive general expressions to calculate chemical potentials. Then, applications of the formalism to a few multicomponent systems based on hard particles with and without attractive forces are given in Sec. V. The results obtained are compared with those from Percus-Yevick and scale particle theories. In Sec. VI we extend the theory to include chemical reactions in the gas. The conclusions are presented in Sec. VII.

II. GAS STATES

The approach developed here is inspired by the variety of spatial patterns shown by fluids where the particles have different types of interactions. The main assumption that will be made is that the spatial structure of a gas in equilibrium can be described by an appropriate division of the space among the particles. The study of single-component fluids at low densities [13] has shown that the volume v assigned to a particle depends on the interactions the particle has with the closest neighbor. In Sec. V we give a formal definition of the closest neighbor. According to the mentioned result, the generalization of the formalism to multicomponent fluid systems (mixtures), requires that the particle population N_i of each chemical species i be divided into subgroups or subclasses in accordance with the chemical species of the nearest neighbor, i.e.,

$$N_i = N_{i1} + N_{i2} + N_{i3} + \dots \quad (1)$$

where the subindices $1, 2, 3, \dots$ specify the various chemical species of the closest neighbors. We consider that for any reference particle in whatever configuration of N particles, there is one and only one j th neighbor, with $1 \leq j \leq N-1$. This means that if there is degeneracy where two particles can be equidistant from the reference, one of them will be designated as the j th neighbor arbitrarily, while the other will be the $(j+1)$ th neighbor. In what follows we shall use the subindex ilv for a particle of class i that has individual available volume v , whose nearest neighbor is of class l . The state of the gas will then be described by the following collections:

$$\begin{bmatrix} N_{11v} & N_{12v} & \dots \\ N_{21v} & N_{22v} & \dots \\ \vdots & \vdots & \ddots \end{bmatrix} \quad (0 \leq v \leq V), \quad (2)$$

where $N_{ilv}dv$ is the number of particles ilv with available individual volumes ranging from v to $v+dv$. The physically acceptable states in (2) must obey the particle number N_{il} and

gas volume V conservation conditions given by

$$N_{il} = \int_0^V N_{ilv} dv, \quad (3)$$

$$V = \sum_{il} \int_0^V v N_{ilv} dv. \quad (4)$$

Thus, the individual volume v assigned to each particle acts as an attribute inherent to each particle and the sum of v spaces is equivalent to the entire volume of the gas. This space partition does not involve any knowledge of particle positions, since the assignment of a v volume to each particle does not carry any information on the particle coordinates.

III. HELMHOLTZ FREE ENERGY

To evaluate the free energy of the gas we use a composition of translation-, configuration-, and interaction-dependent terms,

$$F = F_{\text{trans}} + F_{\text{conf}} + U_{\text{int}}, \quad (5)$$

which is suitable for a large variety of fluids [22]. The first two contributions to F can be written, respectively, as

$$F_{\text{trans}} = \sum_{il} \int_0^V \frac{N_{ilv}}{\beta} \ln \left(\frac{\lambda_i^D}{V} \right) dv, \quad (6)$$

$$F_{\text{conf}} = \sum_{il} \int_0^V \frac{N_{ilv}}{\beta} \ln \left(\frac{N_{ilv} V}{N_i} \right) dv, \quad (7)$$

where $\beta = (kT)^{-1}$, k is the Boltzmann constant, T is the temperature, and λ_i is the thermal wavelength of particles of class i . F_{conf} was obtained following the steps described in Ref. [13], except that in the present case was done for a gas mixture. For the multicomponent system, we have then the total number of ways W to generate a set $\{N_{ilv}\}$ of occupation numbers from the individual complexions W_i is $W = \prod_i W_i$, where

$$W_i = N_i! \prod_{lv} \frac{(dv/V)^{N_{ilv}}}{(N_{ilv} dv)!}. \quad (8)$$

Therefore, according to Ref. [13] the configuration entropy is

$$S_{\text{conf}} = k \ln W = -k \sum_{il} \int_0^V N_{ilv} \ln \left(\frac{N_{ilv} V}{N_i} \right) dv, \quad (9)$$

which finally determines (7), since $F_{\text{conf}} = -TS_{\text{conf}}$.

The interaction can be generalized in the same way as follows:

$$U_{\text{int}} = \sum_{il} \int_0^V N_{ilv} \left(\sum_j \frac{N_j \phi_{ilv,j}}{2V} \right) dv, \quad (10)$$

where the pair-interaction factors $\phi_{ilv,j}$ are

$$\phi_{ilv,j} = \int_0^{V'} u_{ilv,j}(\omega) g_{ilv,j}(\omega) d\omega. \quad (11)$$

In (11), $u_{ilv,j}$ is the interaction potential between a particle of class ilv and another of class j . The distribution function of particles j with respect to the reference particle ilv is written as $g_{ilv,j}$. We note that the integration variable ω in Eq. (11) is a spherical volume centered at the particle of class i and that V' denotes the minimum ω volume able to enclose the entire volume of the mixture. The total free energy of the gas mixture is then

$$F = \sum_{il} \int_0^V N_{ilv} \left[\frac{1}{\beta} \ln \left(\frac{N_{ilv} \lambda_i^D}{N_i} \right) + \sum_j \frac{N_j \phi_{ilv,j}}{2V} \right] dv. \quad (12)$$

IV. EQUILIBRIUM STATES

The equilibrium distributions N_{ilv} are obtained by minimizing the free energy (12) and taking into account the conservation conditions given by Eqs. (3) and (4). The minimizing procedure must take into account that the variations δN_{ilv} affect the total particle populations of each species according to the relation

$$N_j = \sum_m \int_0^V N_{jmv} dv. \quad (13)$$

We thus obtain for the state of equilibrium

$$N_{ilv} = \frac{N_i}{\lambda_i^D} \exp[-\beta(\gamma v - \mu_{il} + \epsilon_{ilv} + \epsilon_i)], \quad (14)$$

where

$$\epsilon_{ilv} = \sum_j \frac{N_j \phi_{ilv,j}}{2V} \quad (15)$$

and

$$\epsilon_i = \sum_{jm} \frac{1}{2V} \int_0^V N_{jmv} \phi_{jmv,i} dv. \quad (16)$$

In Eq. (14), μ_{il} and γ are the Lagrange multipliers corresponding to conditions (3) and (4), respectively. Accordingly, the potentials μ_{il} determine the total population of particles i and their redistribution into subsets as a function of the nearest neighbor class. The variable γ determines the distribution of individual available volumes v .

It is useful to note that the total interaction energy can also be written as

$$U_{\text{int}} = \sum_i N_i \epsilon_i = \sum_{il} \int_0^V N_{ilv} \epsilon_{ilv} dv, \quad (17)$$

which enable us to see that ϵ_i is the average energy due to all interactions the particle of class i has with the gas, while ϵ_{ilv} represents the interaction energy of the ilv particle with the gas. Finally, using (14) and (12) we can write the equilibrium free energy for multicomponent gases in the Eulerian form

$$F = -\gamma V + \sum_{il} \mu_{il} N_{il} - U_{\text{int}}. \quad (18)$$

A. Lagrange parameters

Relation (A5) obtained in the Appendix and (18) help us to show easily that μ_{il} behaves as a thermodynamic potential associated to the N_{il} population,

$$\mu_{il} = \left. \frac{\partial F}{\partial N_{il}} \right|_{T,V,N_{jm \neq il}}. \quad (19)$$

Similarly, making use of (18) and (A10) we find that γ relates to the pressure P in the already known way for single-component fluids [13],

$$P = \gamma + \frac{U_{\text{int}}}{V}, \quad (20)$$

i.e., the gas pressure is the sum of γ and the interaction-energy density.

B. Chemical potentials

The chemical potential corresponding to i -class particles is

$$\mu_i = \left. \frac{\partial F}{\partial N_i} \right|_{T,V,N_{j \neq i}}. \quad (21)$$

The substitution of (18) and (21) and the use of relation (A13) lead to the following expression of μ_i in terms of potentials μ_{il} ,

$$\mu_i = \sum_{lm} \mu_{lm} \left. \frac{\partial N_{lm}}{\partial N_i} \right|_{T,V,N_{j \neq i}}. \quad (22)$$

In fluids with low enough density, it is expected that the splitting up of the N_i populations into subgroups N_{il} [Eq. (1)] be determined by the mole fractions $x_l = N_l/N$ of species present in the gas. This means that the population of particles i having as closest neighbors the class l particles is proportional to the total population of i particles and to the abundance of l -class particles,

$$N_{il} = \frac{N_l N_i}{N} = x_l N_i. \quad (23)$$

We can also say that the probability of a particle had an l class as the closest neighbor is given simply by the abundance of l species. In this case (22) becomes

$$\mu_i = \sum_l (\mu_{il} + \mu_{li}) x_l - \sum_{lm} \mu_{lm} x_l x_m. \quad (24)$$

It is easy to show that if μ_{il} is given by the sum of two terms $f_i + g_l$, i.e., one term that depends on the class i and the other on l , it will be $\mu_i = f_i + g_i$. This is what happens in a mixture of ideal gases, as it is shown in what follows. Let us note that introducing (14) into (3) leads to the useful relation

$$N_{il} = \lambda_i^{-D} N_i Z_{il} e^{\beta \mu_{il}}, \quad (25)$$

where

$$Z_{il} = \int_0^V \exp[-\beta(\gamma v + \epsilon_{ilv} + \epsilon_i)] dv. \quad (26)$$

On the one hand, for noninteracting gases (hereafter identified with the superscript *), we have

$$Z_{il}^* = (\beta \gamma)^{-1} = n^{-1}, \quad (27)$$

which is obtained from (4) and the estimation is done for the thermodynamic limit $(N, V) \rightarrow \infty$ with $n \equiv N/V = \text{constant}$. Therefore, for a mixing of gases it becomes

$$\mu_{il}^* = kT \ln \left(\frac{N_l \lambda_i^D}{V} \right), \quad (28)$$

which through Eq. (24) yields the following exact result:

$$\mu_i^* = kT \ln \left(\frac{N_i \lambda_i^D}{V} \right). \quad (29)$$

On the other hand, for interacting fluids, relation (26) gives

$$Z_{il} = (\beta \gamma)^{-1} q_{il} e^{-\beta \epsilon_i}, \quad (30)$$

with

$$q_{il} = \int_0^\infty e^{-(x + \beta \epsilon_{ilv})} dx, \quad (31)$$

where $x = \beta \gamma v$. In general, if interactions in the gases are fairly low, factors (31) will be $q_{il} \approx 1$. In fact, $q_{il} \rightarrow 1$ if $\epsilon_{ilv} \rightarrow 0$. Using the condition (23) one obtains

$$\frac{\mu_{il}^{ex}}{kT} = \ln \left(\frac{\beta \gamma}{n} \right) + \frac{\epsilon_i}{kT} - \ln q_{il}, \quad (32)$$

$$\frac{\mu_i^{ex}}{kT} = \ln \left(\frac{\beta \gamma}{n} \right) + \frac{\epsilon_i}{kT} - \ln Q_i, \quad (33)$$

in which

$$\ln Q_i = \sum_l x_l \left(\ln(q_{il} q_{li}) - \sum_m x_m \ln q_{im} \right). \quad (34)$$

The excess chemical potentials $\mu_{il}^{ex} = \mu_{il} - \mu_{il}^*$ and $\mu_i^{ex} = \mu_i - \mu_i^*$ are formed by three contributions with specific characteristics. The first right-hand term of Eqs. (32) and (33) represents the deviation of the division of space among particles with respect to that in a perfect gas, i.e., $\beta \gamma \neq n$. This effect is the same for all chemical potentials. The second right-hand term in (32) and (33) gives the contribution due to the potential energy acquired on average by an i -class particle due to its interaction with all the remaining particles in the gas. The third term corresponds to interactions that affect the distribution of individual spaces v , as can be seen from the definition of q_{il} in (31). This last contribution can be significant even for interactions that do not carry energy to the gas, as it is for infinitely strong repulsive forces (see Sec. V).

By virtue of Eq. (33), we can obtain a similar expression to (25) for the total population of a given class

$$N_i = \lambda_i^{-D} N Z_i e^{\beta \mu_i}, \quad (35)$$

where

$$Z_i = (\beta\gamma)^{-1} Q_i e^{-\beta\epsilon_i}. \quad (36)$$

V. HARD PARTICLES

A mixture of hard spheres in D dimensions is characterized by interaction potentials described by

$$u_{ilv,j}(\omega) = \begin{cases} \infty, & \omega \leq a_{ij}, \\ 0, & \omega > a_{ij}, \end{cases} \quad (37)$$

with $a_{ij} = 2^D \sigma_{ij}$, where σ_{ij} is the volume of a D -dimensional sphere with diameter $(d_i + d_j)/2$, being d_i and d_j the respective diameters of particles of classes i and j . The interaction does not depend neither on the l -class neighbor nor on the available volume. To identify the available volume v of a given particle we adopt as reference the results found in Ref. [13] for single-component fluids. We adopt then as ansatz that for low particle densities the available volume is the ideal volume v^* (i.e., v of noninteracting particles, see Sec. I) reduced by an amount a_{il}^* that depends on the repulsion between the particle and its neighbor with the shortest contact distance (hereafter *nscd*):

$$v = v^* - a_{il}^*. \quad (38)$$

Other interpretations than (38) are also possible. However, the results that are obtained in the present section strongly support the choice given in (38). As a consequence of this interpretation, a particle of class $j \neq l$ with $a_{ij} < a_{il}$ can have its center at a shorter distance from the center of particle i than the particle l .

The identification of a volume per particle enables us to specify the form of the distribution function of pairs (hereafter *pdf*) $g_{ilv,j}(\omega)$ for low densities. Notice that $g_{ilv,j}(\omega)d\omega$ gives the probability of finding a particle of class j located between the surfaces of spheres ω and $\omega + d\omega$ both centered in a particle ilv . According to the results obtained in Ref. [13] for single-component fluids, we deduce that the *pdf* with $j=l$ has a contribution due to the *nscd* given by a Dirac delta function $\delta(x)$ evaluated on the *nscd* center and divided by the density of l -class particles. In fluids of low density, the contribution to the *pdf* due to the remaining particles j can be approximated with a Heaviside step function $\Theta(x)$ [$\Theta(x)=1$ for $x \geq 0$ and $\Theta(x)=0$ when $x < 0$], which implies that the position of these particles is uncorrelated with that of the reference ilv one. Thus,

$$g_{ilv,j}(\omega) = \frac{\delta_{jl}}{n_l} \delta(\omega - v - a_{il}^*) + \Theta(\omega - v - a_{il}^* + a_{il} - a_{ij}). \quad (39)$$

The terms in the argument of the step function warrant that the *nscd* is a l -class particle. The Kronecker delta symbol δ_{jl} ensures that the contribution due to *nscd* is taken into account only if $j=l$. Introducing Eqs. (37) and (39) into Eq. (11) we obtain

$$\phi_{ilv,l} = \begin{cases} \infty, & v \leq b_{il}, \\ 0, & v > b_{il}, \end{cases} \quad (40)$$

and

$$\phi_{ilv,j \neq l} \equiv 0, \quad (41)$$

where

$$b_{il} = a_{il} - a_{il}^*. \quad (42)$$

It follows then that

$$\epsilon_{ilv} = \begin{cases} \infty, & v \leq b_{il}, \\ 0, & v > b_{il}, \end{cases} \quad (43)$$

while $\epsilon_i = 0 \forall i$. In the thermodynamic limit, Eqs. (3) and (4) yield

$$\mu_{il} = kT \left[\frac{b_{il}n}{1-bn} + \ln \left(\frac{n_{il}\Lambda_i^D}{n_i} \frac{n}{1-bn} \right) \right], \quad (44)$$

$$n_{ilv} = \Theta(v - b_{il}) n_{il} \beta \gamma \exp[-\beta \gamma (v - b_{il})], \quad (45)$$

$$\beta \gamma = \frac{n}{1-bn}, \quad (46)$$

where we have written

$$bn = \sum_{il} b_{il} n_{il}. \quad (47)$$

As it is expected, the gas does not store interaction energy, which implies that $U_{int} = 0$ and thus $\gamma = P$. From the comparison of Eq. (46) with the corresponding virial expansion for mixtures of hard spheres [16], enables us to make the following identifications:

$$b_{il} = 2^{D-1} \sigma_{il}, \quad (48)$$

$$n_{il} = x_l n_i. \quad (49)$$

Relation (48) is nothing but an extension of previous results found for single-component fluids, while (49) confirms the relation already established in Eq. (23). Since $\sigma_{il} = \sigma_{li}$ the quantities a_{il} , b_{il} , and a_{il}^* are symmetric in the indices il . In particular, $a_{il}^* = a_{li}^* = 2^{D-1} \sigma_{il}$, so that the volume of a hard sphere is reduced with respect to the ideal value v^* by an amount that does not depend on which of both, the reference or the *nscd* particle, is the largest. Nevertheless, as it is expected, a big *nscd* reduces more the space v of a given particle than a small *nscd*.

On the other hand, from Eqs. (24) and (44) we obtain the excess chemical potential for hard spheres of species i that is given by

$$\frac{\mu_i^{ex}}{kT} = -\ln(1-bn) + \frac{2 \sum_l b_{il} n_l - bn}{1-bn}, \quad (50)$$

which in particular for $D=1$ reduces to

$$\frac{\mu_i^{ex}}{kT} = -\ln \left(1 - \sum_l \sigma_{il} n_l \right) + \frac{\sigma_{il} n}{1 - \sum_l \sigma_{il} n_l}. \quad (51)$$

Equation (46) is exact for $D=1$ [23,24] and it gives only an approximate solution for $D > 1$. However, it gives the correct asymptotic behavior for $n \rightarrow 0$. This is shown explicitly in

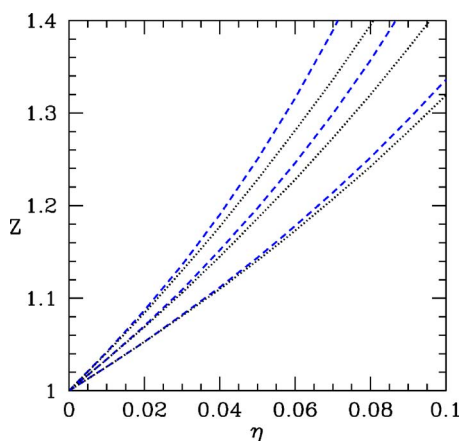


FIG. 1. (Color online) The compressibility Z factor calculated with Eq. (46) (dashed lines) and Percus-Yevick results [25] (dotted lines) as a function of the packing fraction η for 3D binary mixtures with $x_1=0.5$ and $d_2/d_1=0.01, 0.4,$ and 1.0 (from bottom to top).

Fig. 1, where the compressibility factor $Z=P/(nkT)$ is calculated with Eq. (46) and compared with the Percus-Yevick (PY) approximation [25] for a three-dimensional binary mixture, as a function of the packing fraction $\eta=\sum_i n_i \sigma_{ii}$ which gives the fraction of the total volume occupied by the hard particles. Since we compare our results with those of the PY theory, one of the most successful theoretical approaches in studies of fluids, let us recall that it is based on an approximate integral equation of the radial distribution function from which the thermodynamics of hard-body systems follows as a by product. In few cases, it can be solved analytically, e.g., mixture of hard spheres, and the solutions obtained are very close to those issued from computer simulation [22].

Likewise, Eq. (51) is exact for hard rods [27]. Equation (50) provides the correct low-density behavior of the excess chemical potential for $D>1$. The latter is illustrated in Figs. 2 and 3, which show the comparisons of our results obtained for $D=3$ with those issued from the scale particle theory

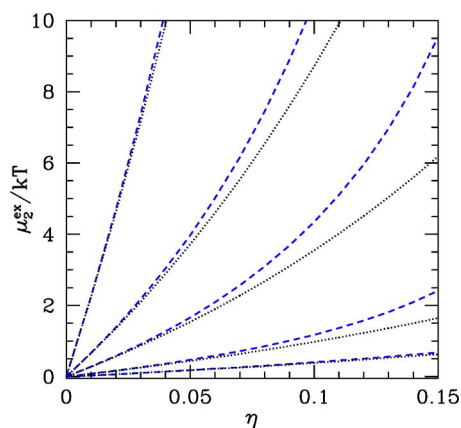


FIG. 2. (Color online) Excess chemical potentials of a diluted solution (here species 2) calculated with Eq. (50) (dashed lines) and those from the scale particle theory [26] (dotted lines) as a function of the packing fraction η for 3D binary mixtures with $x_2=10^{-5}$ and $d_2/d_1=0.5, 1.0, 2.0, 3.0,$ and 5.0 (from bottom to top).

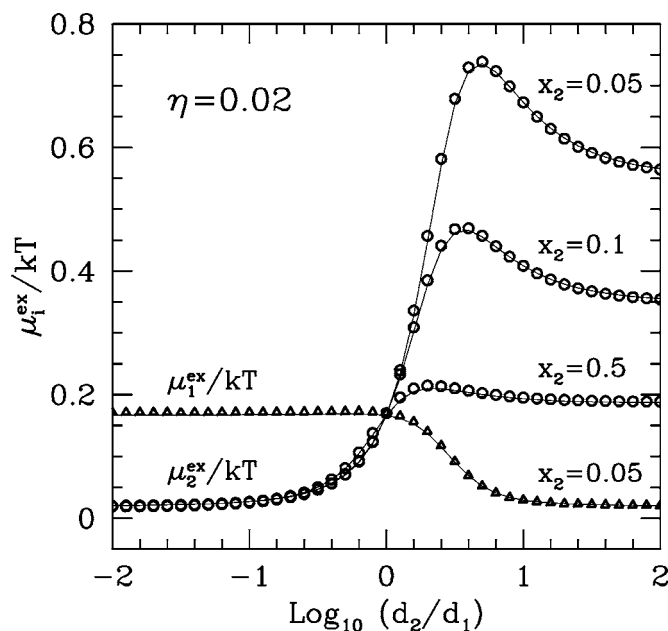


FIG. 3. Excess chemical potentials obtained with Eq. (50) (symbols) and Percus-Yevick theory results [27] (lines) as a function of the diameter ratio d_2/d_1 for 3D binary mixtures with $\eta=0.02$ and $x_2=0.05, 0.1,$ and 0.5 .

[26], which is correct for a solute infinitely diluted and with the PY solutions found by Lebowitz [25], respectively. It is important to note that all expressions derived for mixtures of hard spheres are exact up to the second term in the virial expansion. Finally, we can conclude that the achievement of agreements shown in Figs. 1–3 confirm the appropriateness of the closure relations (23) and (38) adopted, where $a_{il}^*=2^{D-1}\sigma_{il}$. Since our work aims at giving a detailed representation of complex gases at low densities ($\eta<0.01$), the results we have obtained can be considered as very satisfactory.

A. Pair-distribution functions

From detailed $g_{ilv,j}$ functions it is possible to calculate the averaged *pdf* with the occupational numbers n_{ilv} (see Ref. [13]). For example, the probability of finding a j particle between the spherical surfaces ω and $\omega+d\omega$ centered in a i particle, regardless of its available volume, whose n_{scd} is an l particle, defines a *conditional pair distribution function cpdf* which is given by

$$g_{il,j}(\omega) = \frac{1}{n_{il}} \int_0^\infty g_{ilv,j}(\omega) n_{ilv} dv. \quad (52)$$

The traditional g_{ij} can be computed from the summation over all species of *cpdf* appropriately weighted by the probability of finding a *nlcd* of a given class,

$$g_{ij}(\omega) = \sum_l x_l g_{il,j}(\omega). \quad (53)$$

For mixtures of hard spheres, Eqs. (52) and (53) give, respectively,

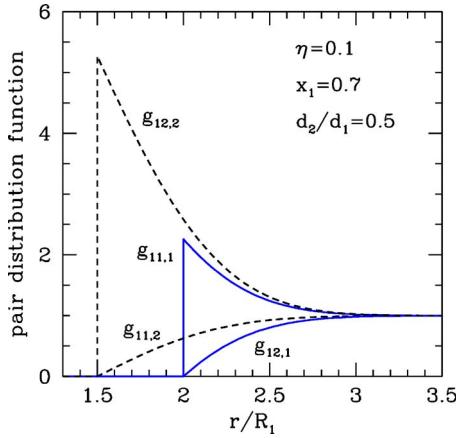


FIG. 4. (Color online) Conditional pdf from Eq. (54) as a function of the normalized radial distance r/R_1 ($R_1=d_1/2$ is the radius of a particle of species 1) for a 3D binary mixture with $\eta=0.1$, $x_1=0.7$, and $d_2/d_1=0.5$.

$$g_{il,j}(\omega) = \Theta(\omega - a_{ij}) \left[1 + \left(\delta_{jl} \frac{\beta\gamma}{n_l} - 1 \right) e^{-\beta\gamma(\omega - a_{ij})} \right], \quad (54)$$

$$g_{ij}(\omega) = \Theta(\omega - a_{ij}) \left[1 + \frac{bn}{1 - bn} \exp\left(-\frac{n(\omega - a_{ij})}{1 - bn} \right) \right]. \quad (55)$$

Equations (54) and (55) are approximations suitable for low densities, because the function $g_{ilv,j}$ in Eq. (39) takes into account explicitly only the correlations between the reference particle and its *nscd*. However, they contain the most important deviations with respect to the solutions for perfect gases.

To our knowledge, this is the first time that the *cpdf* are suggested and calculated for mixtures of hard spheres. Figure 4 shows some *cpdf* for a binary mixture with $\eta=0.1$ and $x_1=0.7$. In the chosen example, particles of class 1 have a diameter twice as large as those of class 2. Functions $g_{il,j}$ become zero for distances r between particles i and j shorter than the contact distances, as it happens for the conventional *pdf* g_{ij} . Nevertheless, contrary to functions g_{ij} , the behavior of *cpdf* at moderate distances can be strongly affected due to the information on the *nscd* class carried by the reference particle. Thus, up to the present level of approximations, the function $g_{12,2}$ grows above 1 for small values of r ($r > 1.5R_1$, $r \rightarrow 1.5R_1$, where R_1 is the radius of class 1 spheres). This is due to the fact that the probability of finding a particle of class 2 at a distance $r \approx 1.5R_1$ from another of class 1 augments if it happens that the latter has a *nscd* of class 2. This augmentation concerns the nonconditioned probability of finding a class 2 particle and so, it is higher the lower is the abundance of the considered species. Conversely, for the same range of distances, the function $g_{11,2}$ decreases because the possibility of *nscd* be of class 2 is removed.

The results corresponding to a mixture of ideal gases are contained naturally in the expressions (54) and (55). In this case, the results are exact. For permeable spheres, i.e., a_{ij}

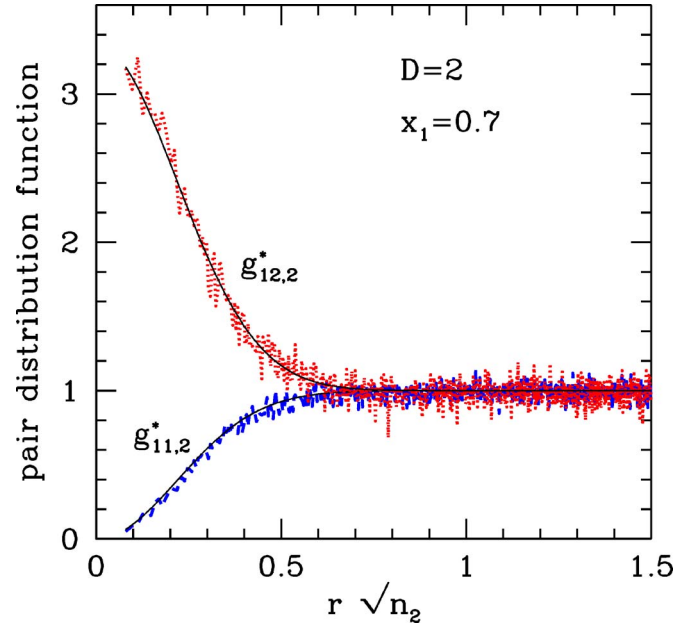


FIG. 5. (Color online) Conditional pdf computed with Eq. (54) (full lines) as a function of the dimensionless radial distance $r\sqrt{n_2}$ (in units of the mean distance between particles of species 2) for a 2D binary mixture of perfectly permeable particles at $x_1=0.7$. The results obtained from numerical simulations with 10^5 Poissonian points are shown for comparison (dotted lines).

$=b_{ij}=a_{ij}^*=0$, the expected correct result $g_{ij}^*=1 \forall i,j$ is obtained. Moreover,

$$g_{il,j}(\omega) = \begin{cases} 1 - e^{-n\omega} & (j \neq l), \\ 1 + (x_l^{-1} - 1)e^{-n\omega} & (j = l). \end{cases} \quad (56)$$

Figure 5 shows some *cpdf* corresponding to a binary bidimensional mixture predicted by Eq. (56) (full lines), which are in excellent agreement with the results obtained from numerical simulations (dotted lines) based on two sets of uncorrelated points created by a random number generator.

B. van der Waals mixture

The van der Waals model for a mixture can be obtained by adding to the repulsive forces [Eq. (37)] a generalized Kac type attraction potential,

$$u_{ilv,j}(\omega) = \begin{cases} \infty, & \omega \leq a_{ij}, \\ -\epsilon_{ij}\gamma^* J(\gamma^*\omega), & \omega > a_{ij}, \end{cases} \quad (57)$$

where $\epsilon_{ij} \geq 0$ are constants and J is a function that satisfy the condition $\int_0^\infty J(\omega)d\omega=1$. In the limit $\gamma^* \rightarrow 0$ it becomes

$$\phi_{ilv,l} = \begin{cases} \infty, & v \leq b_{il}, \\ -\epsilon_{il}, & v > b_{il}, \end{cases} \quad (58)$$

and

$$\phi_{ilv,j \neq l} = -\epsilon_{ij}, \quad (59)$$

so that

$$\epsilon_{ilv} = \begin{cases} \infty, & v \leq b_{il}, \\ -\frac{1}{2} \sum_j \epsilon_{ij} n_j, & v > b_{il}. \end{cases} \quad (60)$$

The attracting forces modify the chemical potentials and the total interaction energy of the gas, so that it results in

$$\mu_{il} = kT \left[\frac{nb_{il}}{1-nb} + \ln \left(\frac{n_{il} \lambda^D}{n_i} \frac{n}{1-nb} \right) \right] - \sum_j \epsilon_{ji} n_j \quad (61)$$

and

$$\frac{U_{\text{int}}}{V} = -\frac{\epsilon n^2}{2}, \quad (62)$$

where

$$b = \sum_{ij} x_i x_j b_{ij} \quad (63)$$

and

$$\epsilon \equiv \sum_{ij} x_i x_j \epsilon_{ij}. \quad (64)$$

Nevertheless, Eqs. (45) and (46) remain unchanged as it happens for single-component fluids [13]. We then see that using Eq. (20) the known relation $P = (nkT)/(1-nb) - \epsilon n^2/2$ is recovered. Relations (63) and (64) are often used as mixing rules which relate the properties of the pure component models to those of mixtures in extended models. They are considered adequate for mixtures of monopolar compounds [28–30] and vapor-liquid phenomena [31].

C. Attractive hard spheres

A simple model of hard spheres having short-range attractive forces, as opposite to the long-range van der Waals model, is obtained by adding a square-well potential at the edge of a repulsive nucleus,

$$u_{ilv,j}(\omega) = \begin{cases} \infty, & \omega \leq a_{ij}, \\ -\epsilon_{ij}, & a_{ij} < \omega < a_{ij} + \xi, \\ 0, & \omega \geq a_{ij} + \xi, \end{cases} \quad (65)$$

where ξ is a characteristic attractive volume surrounding the a_{ij} volume of the repulsive nucleus. For simplicity we adopt a value of ξ independent of the considered pair of particles. This potential is used often to model the interactions among colloidal particles and protein molecules [32–34], which commonly have attractive forces in the very nearest vicinity of their surfaces ($\xi \ll a_{ij}$). With Eq. (65), Eqs. (11) and (15) lead to

$$\phi_{ilv,j} = \begin{cases} \infty, & v \leq b_{il}, \\ -\epsilon_{ij} \left(\frac{\delta_{lj}}{n_l} + b_{il} + \xi - v \right), & b_{il} < v < b_{il} + \xi, \\ 0, & v \geq b_{il} + \xi \end{cases} \quad (66)$$

and

$$\epsilon_{ilv} = \begin{cases} \infty, & v \leq b_{il}, \\ -\frac{\epsilon_{il}}{2} - B_i(b_{il} + \xi - v), & b_{il} < v < b_{il} + \xi, \\ 0, & v \geq b_{il} + \xi, \end{cases} \quad (67)$$

where

$$B_i = \sum_j \frac{\epsilon_{ij} n_j}{2}. \quad (68)$$

The state equations that result from the particle and volume conservation relations (3) and (4) are

$$\mu_{il} = kT \left[\beta \gamma b_{il} + \ln \left(\frac{\beta \gamma n_{il} \lambda^D}{n_i X_{il}} \right) \right] + \epsilon_i, \quad (69)$$

$$\beta \gamma = \sum_{il} n_{il} \frac{Y_{il}}{X_{il}}, \quad (70)$$

where we have

$$X_{il} = e^{-\beta \gamma \xi} + \beta \gamma e^{\beta(\epsilon_{il}/2 + B_i \xi)} \left(\frac{1 - e^{-\beta(\gamma + b_i) \xi}}{\beta(\gamma + B_i)} \right), \quad (71)$$

$$Y_{il} = [1 + \beta \gamma (b_{il} + \xi)] e^{-\beta \gamma \xi} + \left(\frac{\gamma}{\gamma + B_i} \right)^2 e^{\beta(\epsilon_{il}/2 + B_i \xi) \xi} \{1 + \beta(\gamma + B_i) b_{il} - [1 + \beta(\gamma + B_i)(b_{il} + \xi)] e^{-\beta(\gamma + B_i) \xi}\}. \quad (72)$$

Besides, the v -occupation number distribution is given by

$$n_{ilv} = n_{il} \frac{\beta \gamma}{X_{il}} e^{-\beta[\gamma(v - b_{il}) + \epsilon_{ilv}]}. \quad (73)$$

We can also obtain an analytic expression for the interaction energy,

$$\frac{U_{\text{int}}}{V} = \sum_{il} \frac{\beta \gamma n_{il}}{X_{il}} e^{\beta(\epsilon_{il}/2 + B_i \xi)} \times \left[-\left(\frac{\epsilon_{il}}{2} + B_i \xi \right) \left(\frac{1 - e^{-\beta(\gamma + B_i) \xi}}{\beta(\gamma + B_i)} \right) + B_i \left(\frac{1 - [1 + \beta(\gamma + B_i) \xi] e^{-\beta(\gamma + B_i) \xi}}{[\beta(\gamma + B_i)]^2} \right) \right]. \quad (74)$$

It can be interesting to have limiting expressions of these equations for small enough values of ξ . Keeping only the zero and first order terms, we derive

$$X_{il} = 1 + \beta \gamma \xi (e^{\beta \epsilon_{il}/2} - 1), \quad (75)$$

$$Y_{il} = 1 + \beta \gamma b_{il} + (\beta \gamma)^2 \xi b_{il} (e^{\beta \epsilon_{il}/2} - 1). \quad (76)$$

If also the potential wells are the same, $\epsilon_{il} = \epsilon \forall (i, l)$, the state equation (70) reduces to a quadratic relation in $\beta \gamma$,

$$(\beta \gamma)^2 \xi (e^{\beta \epsilon/2} - 1) + \beta \gamma = \frac{n}{1 - bn}, \quad (77)$$

where $b = \sum_{il} x_i x_l b_{il}$. When the thickness ξ or the depth ϵ of the potential well tend to zero, the state equation (77) recovers the form corresponding to a mixture of pure hard spheres. The same result is obtained for high enough temperatures, $kT \gg \epsilon$.

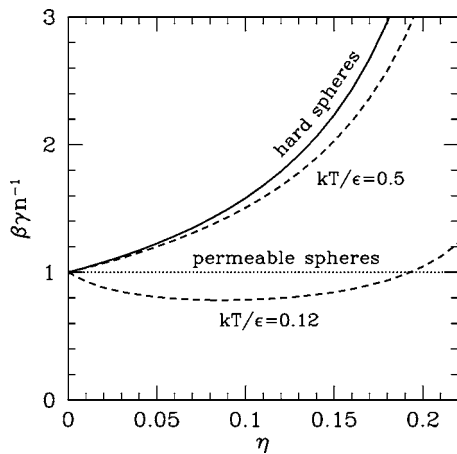


FIG. 6. Factor $\beta\gamma n^{-1}$ as a function of the packing fraction for 3D binary mixtures of spheres with $x_1=0.7$ and $d_2/d_1=0.5$. *Dotted line*, perfectly permeable spheres; *full line*, hard spheres and van der Waals fluid; *dashed lines*, square-well fluid with $\xi/\sigma=0.2$ (σ is the mean volume of a particle) and reduced temperatures $kT/\epsilon=0.12$, 0.5. The result for pure hard spheres is obtained for $kT/\epsilon \rightarrow \infty$.

D. Space distributions

The thermodynamic variable γ has the function of adjusting the allotment of space among particles in order to satisfy the mathematical requirements of space filling established by (4). In mixtures of noninteracting particles the occupation number distributions n_{ilv} depends on the individual volume per particle v through the exponential $\exp(-\beta\gamma v)$. In this case, the scale factor $\beta\gamma$ is equivalent to the total number density of particles n . Obviously, the allotment of space is not homogeneous. Most particles have smaller available volumes than the average volume per particle, n^{-1} , while the statistical partition of big volumes is low.

The particle interactions change the assignment of the volume v for each particle and thus they change the occupation numbers n_{ilv} , as compared to those for ideal gases. Therefore, the interactions also affect the γ values. In Fig. 6 we have plotted $\beta\gamma n^{-1}$ as a function of the packing fraction η for perfectly permeable spheres (dotted line), pure hard spheres (full line), and hard spheres with square-well potentials (dashed lines). Notice that $\beta\gamma n^{-1}$ is a measure of γ in units of perfect gas values. Figures 7 and 8 show occupation number distributions n_{ilv} for binary mixtures of pure and attractive hard spheres, based on Eqs. (45) and (73), respectively. The lower cutoff value for each curve corresponds to the smallest volume v permitted by the repulsion between a hard sphere and its $nscd$, as given by Eq. (38). The square-well potential yields the peaks observed in Fig. 8. If we make abstraction of the normalization constants—area under the curves representing the n_{il} population—the peak height of curves n_{ilv} vs v in Figs. 7 and 8 depend on the abundance of the corresponding pairs il . In the frame of models of mixtures considered here the distributions n_{12v} and n_{21v} are coincident.

In a hard sphere mixture, the repulsions among the particles produce an increase of the mean volume per particle. As a consequence, at given temperature and density the

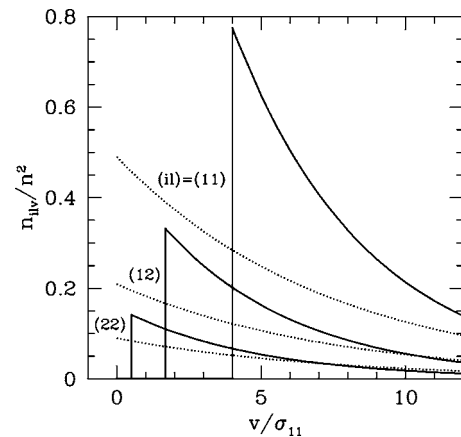


FIG. 7. Dimensionless double densities n_{ilv}/n^2 as a function of the available volume per particle (in units of volume σ_{11} of a particle of class $i=1$) for a 3D binary mixture of hard spheres with $\eta=0.1$, $x_1=0.7$, and $d_2/d_1=0.5$ (solid lines). Results corresponding to fully penetrable spheres are shown by comparison (dotted lines).

value of γ must increase (full line in Fig. 6) to warrant the occupation distributions n_{ilv} be correctly displaced towards higher values of v (full lines in Fig. 7). On the contrary, the attractive forces of finite range in a square-well fluid, increase the population of particles with small individual volumes (full lines in Fig. 8) and reduce the values of γ as compared to those of pure hard spheres (dashed lines in Fig. 6). These changes depend on the temperature value. Low temperatures favor the particle adherence and thus increase the occupation number of low available volume.

The long-range interactions of Kac type analyzed in Sec. VB are such that the magnitude of the interaction of each particle with the remaining medium does not depend on the nearness of its neighbors. Hence, the attractive forces have no incidence on the space occupation distribution n_{ilv} , neither on γ , both being equivalent to those in a mixture of pure hard spheres and hence independent of the temperature.

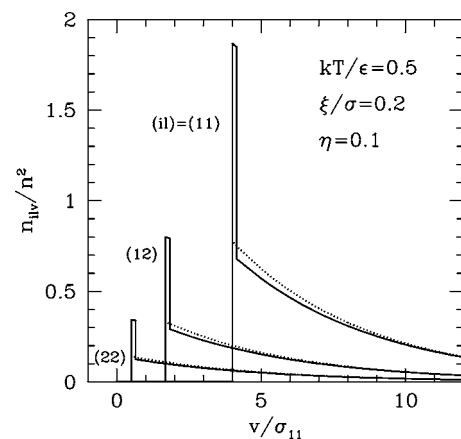


FIG. 8. Dimensionless double densities n_{ilv}/n^2 as a function of the available volume per particle (in units of volume σ_{11} of a particle of class $i=1$) for a 3D binary mixture of attractive hard spheres with $\eta=0.1$, $x_1=0.7$, $d_2/d_1=0.5$, $\xi/\sigma=0.2$, and $kT/\epsilon=0.5$ (solid lines). Results for pure hard spheres are shown by comparison (dotted lines).

It is useful to point out that, for ideal and pure hard-sphere mixtures, the quantity $\beta\gamma n^{-1}$ coincides with the compressibility factor $Z=P/nkT$ since these gases cannot store interaction energy and, therefore, γ is equivalent to the gas pressure P . It is not true for the van der Waals and square-well models, because they have a non-negligible interaction energy, so that γ and P differ as described by relation (20).

VI. CHEMICAL EQUILIBRIUM

In this section we extend the theory somewhat to include cases where chemical reactions can occur. In this case, the total free energy contains a contribution given by the summation of all particle internal energies,

$$E = \sum_i N_i E_i = \sum_{il} \int_0^V N_{ilv} E_i dv, \quad (78)$$

where E_i is the internal energy of a particle i and the reference zero energy is considered the same for all species. If the internal energies E_i are degenerate with multiplicity w_i , then W_i in Eq. (8) becomes

$$W_i = N_i! \prod_{lv} \frac{(w_i dv/V)^{N_{ilv}}}{(N_{ilv} dv)!}. \quad (79)$$

The configuration free energy takes thus the form

$$F_{\text{conf}} = \sum_{il} \int_0^V \frac{N_{ilv}}{\beta} \ln \left(\frac{N_{ilv} V}{w_i N_i} \right) dv. \quad (80)$$

The results obtained in the preceding sections given by (14), (30), and (36) can be generalized now as

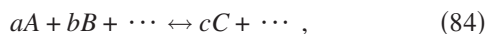
$$N_{ilv} = \frac{N_i}{\lambda_i^D} w_i \exp[-\beta(\gamma v - \mu_{il} + \epsilon_{ilv} + \epsilon_i + E_i)], \quad (81)$$

$$Z_{il} = (\beta\gamma)^{-1} w_i q_{il} e^{-\beta(\epsilon_i + E_i)}, \quad (82)$$

and

$$Z_i = (\beta\gamma)^{-1} w_i Q_i e^{-\beta(\epsilon_i + E_i)}. \quad (83)$$

Now, let us consider the reaction



that involves the species $i=A, B, C, \dots$ and the stoichiometric factors a, b, c, \dots . The equilibrium condition of the reaction is

$$dF = \sum_i \left(\frac{\partial F}{\partial N_i} \Big|_{T, V, N_{j \neq i}} \right) dN_i = \sum_i \mu_i dN_i = 0, \quad (85)$$

which is subject to the conditions

$$\frac{dN_A}{a} = \frac{dN_B}{b} = \dots = -\frac{dN_C}{c} = \dots. \quad (86)$$

The criterion for the equilibrium is therefore

$$a\mu_A + b\mu_B + \dots = c\mu_C + \dots, \quad (87)$$

which through Eq. (35) leads to the relationship among the species abundances,

$$\left(\frac{N_A \lambda_A^D}{N Z_A} \right)^a \left(\frac{N_B \lambda_B^D}{N Z_B} \right)^b \dots = \left(\frac{N_C \lambda_C^D}{N Z_C} \right)^c \dots, \quad (88)$$

that gives the generalized form of the mass-action law.

The results given in this section bring useful tools to study gaseous mixtures, including their chemical equilibrium. Equation (81) sums up the main feats of the present formulation. It enables to describe populations in reacting gases at a level of details attained never before, i.e., to evaluate populations of atoms and molecules in a consistent thermodynamic way, not only by obtaining the density of each species, but giving as well its populations per groups according to the available volume of each particle, where this variable is linked directly with the degree of perturbations experienced by the atoms due to the presence of neighbors. In the preceding work [13] we have foreseen some results that could be obtained with the present theory. For example, it is possible to show that atoms of a given species in a gas do not have all the same effective ionization potential (electronic energy relative to the energy threshold corresponding to free electrons), but can they have a variety of values according to the available volume of particles. The application of the present theory to mixtures of atomic particles with more realistic interaction potentials than considered here will be presented in a forthcoming paper.

VII. CONCLUSIONS

We have developed a mathematical framework in terms of a Helmholtz free-energy model which aims at describing equilibrium properties of D -dimensional multicomponent fluids. This theory is an extension of a former model devoted to one-component fluids and combines free-energy minimization methods with space partitions based on the available volume v to a particle and the occupation number distributions of this variable. Thus we obtain a unified formalism that treats thermodynamics and structure of complex fluids simultaneously.

The theory is presently developed for the case of dilute fluids, where interparticle interactions are evaluated from pair potentials. Two closure relations (23) and (38) are required to obtain a closed formalism. The former is associated to the particle number conservation (3) and provides the probability that a particle had a specific species as the closest neighbor. The second closure relation (38) specifies the available-volume variable and, therefore, is linked to the filling space condition (4). Consequently, unconventional thermodynamic variables were derived by introducing space partitions in the thermostistical analysis of fluids. They are Lagrange's multipliers related to the specific particle number and volume conservations, which describe thus chemical potentials and the pressure, respectively. In addition, we have obtained general expressions for the excess chemical potentials and chemical equilibrium conditions of nonideal fluids, as well as several pair distribution functions.

The theory provides a straightforward way to calculate thermodynamic quantities and structure properties of gas mixtures. As illustrative examples, we have considered several hard sphere systems for which simple analytical expres-

sions were derived. The equations of state obtained for pure hard-sphere systems are in good agreement with the scaled-particle and Percus-Yevick solutions valid for low densities. We reckon that this agreement confirms *a posteriori* the validity of the several approaches adopted. Besides, well-known solutions for van der Waals mixtures were recovered easily by using generalized Kac potentials. We also have derived closed analytical forms for thermodynamic quantities of square-well mixture fluids. These evaluations constitute a reference for future studies of short ranged attractive systems. The influence of repulsive and attractive forces on the space partition among particles was analyzed. The results thus obtained express a close relationship between statistical geometry and statistical mechanics.

The formalism introduced in the present work provides a useful tool to investigate the structure and the effective interactions in chemical complex fluids. It is particularly well suited to study some astrophysical gases where detailed descriptions of species and interactions are required. This occurs, in particular, in atmospheres and circumstellar envelopes, where the density can be hardly higher than some $\eta = 0.01$, so that the approximations for low densities given here can be used safely. We consider that the present theory has many other applications in applied problems of current interest, such as studies of equilibrium properties of colloidal and protein solutions.

Among the most important results obtained in this work, we can quote the following:

(i) A functional (or series of functionals for mixing) contains the entire thermodynamical information of the system and leads to a classification of particles according to their distance to the closest neighbor through the assignment of a given volume available to each particle. So, it is thus possible to distinguish the atoms according to the different degrees of perturbations carried by their neighbors. To our knowledge, there is no other model able to make this distinction up to now.

(ii) The current formalism is able to answer to the following inquiries:

(a) What is the probability of finding a particle of class j at a distance r from another particle of species i whose closest neighbor is of class k , knowing that r , i , j , and k are arbitrary?

(b) Idem as before, but for a neighbor k situated at a given (arbitrary) distance from the particle of class i ?

(iii) The chemical equilibrium of a fluid and the classification of particles according to the distance to the respective closest neighbor, are done simultaneously and self-consistently with the laws of thermodynamics.

(iv) As far as we know, it is the first time that a theory is able to provide thermodynamical variables associated with the distribution of the space between the particles of different chemical species directly. The variables are related to the conventional thermodynamical variables explicitly, such as pressure, chemical potential, etc.

The description level attained by our formalism overrides whatever known preexisting model and constitutes an unparalleled tool to represent chemical mixing at low densities. It also provides conceptual elements on the connection between statistical mechanics and spatial statistics.

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APPENDIX: THERMODYNAMIC IDENTITIES

In what follows we derive three thermodynamic identities which enable us to derive relations (19), (20), and (22). The starting point is the equation that gives the total particle population in terms of the occupation number N_{jmv} ,

$$N = \sum_{jm} \int_0^V N_{jmv} dv. \quad (\text{A1})$$

If in (A1) we replace N_{jmv} by its expression given by (14) and derivate it with respect to a given population N_{il} by keeping constant the temperature, volume and the remaining populations ($N_{jm \neq il}$), we shall obtain

$$\begin{aligned} \sum_{jm} \int_0^V N_{jmv} \left(v \frac{\partial \gamma}{\partial N_{il}} - \frac{\partial \mu_{jm}}{\partial N_{il}} + \frac{\partial \epsilon_{jmv}}{\partial N_{il}} + \frac{\partial \epsilon_j}{\partial N_{il}} \right) dv \\ = V \frac{\partial \gamma}{\partial N_{il}} \sum_{jm} N_{jm} \frac{\partial \mu_{jm}}{\partial N_{il}} + \sum_{jm} \int_0^V N_{jmv} \left(\frac{\partial \epsilon_{jmv}}{\partial N_{il}} + \frac{\partial \epsilon_j}{\partial N_{il}} \right) dv = 0. \end{aligned} \quad (\text{A2})$$

The second line in (A2) was obtained using relations (3) and (4). We also note that

$$\sum_{jm} \int_0^V N_{jmv} \frac{\partial \epsilon_{jmv}}{\partial N_{il}} dv = \sum_{jm} \int_0^V N_{jmv} \frac{\phi_{jmv,i}}{2V} dv = \epsilon_i, \quad (\text{A3})$$

and

$$\sum_{jm} \int_0^V N_{jmv} \frac{\partial \epsilon_j}{\partial N_{il}} dv = \sum_j N_j \frac{\partial \epsilon_j}{\partial N_{il}} = \frac{\partial U_{\text{int}}}{\partial N_{il}} - \epsilon_i. \quad (\text{A4})$$

Equations (A2)–(A4) lead to the identity

$$V \frac{\partial \gamma}{\partial N_{il}} - \sum_{jm} N_{jm} \frac{\partial \mu_{jm}}{\partial N_{il}} + \frac{\partial U_{\text{int}}}{\partial N_{il}} = 0. \quad (\text{A5})$$

Then, Eq. (19) can be obtained easily from relations (18) and (A5). In a similar way, the partial derivative of Eq. (A1) with respect to the volume produces

$$\begin{aligned} \sum_{jm} \int_0^V N_{jmv} \left(v \frac{\partial \gamma}{\partial V} - \frac{\partial \mu_{jm}}{\partial V} + \frac{\partial \epsilon_{jmv}}{\partial V} + \frac{\partial \epsilon_j}{\partial V} \right) dv \\ = V \frac{\partial \gamma}{\partial V} - \sum_{jm} N_{jm} \frac{\partial \mu_{jm}}{\partial V} + \frac{\partial U_{\text{int}}}{\partial V} + C = 0, \end{aligned} \quad (\text{A6})$$

with

$$C = \sum_{jm} \int_0^V N_{jmv} \frac{\partial \epsilon_{jmv}}{\partial V} dv. \quad (\text{A7})$$

In Eq. (A6) we have ignored the terms with $N_{jm(v=V)}$, since they become zero at the thermodynamic limit. According to Eq. (15), we have

$$\frac{\partial \epsilon_{jmv}}{\partial V} = -\frac{\epsilon_{jmv}}{V} + \sum_i \frac{N_i \partial_V \phi_{jmv,i}}{2V}. \quad (\text{A8})$$

In general $\partial_V \phi_{jmv,i} = 0$, so that

$$C = -\frac{1}{V} \sum_{jm} \int_0^V N_{jmv} \epsilon_{jmv} dv = -\frac{U_{\text{int}}}{V}. \quad (\text{A9})$$

Hence, from relation (A6) we obtain the following identity:

$$V \frac{\partial \gamma}{\partial V} - \sum_{jm} N_{jm} \frac{\partial \mu_{jm}}{\partial V} + \frac{\partial U_{\text{int}}}{\partial V} - \frac{U_{\text{int}}}{V} = 0. \quad (\text{A10})$$

Knowing that $P = -\partial F / \partial V$, relation (20) is obtained straightforwardly from Eqs. (18) and (A10).

The procedure followed to obtain relation (A5) can also be used to obtain the partial derivative of Eq. (A1) with respect to the population of class i particles (N_i) by considering constant the temperature, volume and the populations of the remaining species ($N_{j \neq i}$). We then use

$$\frac{\partial U_{\text{int}}}{\partial N_i} = \epsilon_i + \sum_j N_j \partial_{N_i} \epsilon_j \quad (\text{A11})$$

and

$$\frac{\partial \epsilon_{jmv}}{\partial N_i} = \frac{\phi_{jmv,i}}{2V}. \quad (\text{A12})$$

The third identity that we can obtain is

$$V \left. \frac{\partial \gamma}{\partial N_i} \right|_{N_{j \neq i}} - \sum_{jm} N_{jm} \left. \frac{\partial \mu_{jm}}{\partial N_i} \right|_{N_{j \neq i}} + \left. \frac{\partial U_{\text{int}}}{\partial N_i} \right|_{N_{j \neq i}} = 0. \quad (\text{A13})$$

Equation (A13) enables us to find an expression for the chemical potential μ_i in terms of the thermodynamic potentials μ_{jm} [Eq. (22)].

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