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Towards the Development of a Universal Expression for the Configurational Entropy of Mixing

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Abstract: This work discusses the development of analytical expressions for the configurational entropy of different states of matter. The methodology presented in this work is based on identification of the energy independent atomic complexes (clustering of atoms) in the mixture, through careful analysis of the main physical features of the system, and the calculation of their corresponding probabilities. The example of SRO in Nb-H interstitial solid solution is used to illustrate the choice of the atomic complexes and their structural changes with the composition. The possibilities of applying the same formalism to describe gases, liquids, glasses and solid states with the same level of accuracy are discussed. The main challenge involved in reaching this goal is to find a set of atomic complexes which can be used to describe, simultaneously, the basic structural features of liquids, glasses and solids. If the connecting structures near the transition liquid-glass/solid are identified, the desired model that can be applied to all states of matter with the same accuracy and level of description could be developed. This work shows that it is possible to develop such a model, but a major theoretical and computational effort will be required.

Keywords: configurational entropy; analytical expressions; interstitial solid solutions; non-crystalline state of matter, equation of state

PACS Codes: 82.60.Lf, 65.40.gd, 61.72.jj, 61.66.Dk

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1. Introduction

The development of analytical expressions for the configurational entropy of mixing was an active field of research several decades ago. Empirical or theoretical expressions and methods were deduced in each field of condensed matter. Several examples can be found in the literature, such as: i) the expressions of Flory [1] and Huggins [2] for linear polymer solutions, ii) Cluster Variation Method (CVM) [3] and Cluster Site Approximation (CSA) [4] for the study of order-disorder and phase equilibrium in alloys, and iii) the Gibbs and Di Marzio expression [5] for glasses, just to cite some of best known expressions in each field. Each model has its own area of applications and research. For example, CVM can not be applied to polymer solutions and Flory's expression is not suitable for the study of order-disorder in alloys. However, the traditional methodology, based on the calculation of the number of configurations, found severe restrictions in the development of expressions in complex systems, like interstitial solid solutions or liquids and amorphous materials. Although an enormous amount of works has been carried out in both fields of research, the deduction of accurate analytical expressions for the configurational entropy of mixing has been very elusive due to the complicated underlying physics. While the difficulties with interstitial solutions come from the blocking effects, the difficulties with liquids, amorphous materials and glasses are derived from the almost insurmountable task of computing the number of configurations in a system without lattice periodicity. The limitations arise because all previous models compute the number of configurations using the lattice gas model under the following assumptions: i) athermal mixture or non-interacting atoms, atomic complexes, molecules, or associated chemical species, which leave their internal properties unaffected, ii) no superposition among chemical species, iii) the equivalence of all N lattice sites, and iv) the use of a rigid lattice with no distortion and constant volume.

The field of research related to interstitial solid solutions is an illustrative example of the difficulties in computing the configurational entropy of mixing if the assumption of no superposition between chemical species is abandoned. Although there are several analytical expressions which can be used to compute the entropy of mixing in these systems, they are all approximated or limited to low or medium solute concentrations. In addition, they all assume a random distribution of interstitial atoms in the interstitial sub-lattice and, consequently, the interaction between defects is not considered in previous models, i.e. no SRO description is possible. Furthermore, they can not describe the differences between chemical and elastic blocking and their influence on the configurational entropy. It is important to note that there is experimental and theoretical evidence that the random blocking model (RBM) [6] assumed in this kind of solid solutions is not appropriate in a number of systems, such as hcp R-H (R=Sc,Y,Lu) [7-9], bcc Nb-H[10] and Zr-H systems [11].

A similar situation to that of interstitial solutions, as regards the encoding of structural information into a compact expression, is found in liquids, amorphous materials and glasses. In these systems, the lack of periodicity of the atomic arrangements makes the deduction of a universal and unique structural description a very difficult task, leaving many questions unanswered. Consequently, the deduction of an analytical expression for the configurational entropy of mixing of multicomponent systems, valid for any non-crystalline states of matter, remains a largely unsolved problem.

The development of such model just counting the number of configurations is an impractical idea. However, a recent formalism to compute the configurational entropy, based on the identification of energetically independent complexes within the mixture and the calculation of their respective probabilities, offers an opportunity to consider this proposal seriously. The importance of such an idea is not only academic in nature, i.e., the development of a unified description for all states of matter; it originates from the need to develop general expressions with the same level of accuracy for each state of matter. Indeed, it would be desirable to describe liquids, glasses and solid states with the same model and level of accuracy so as to obtain a precise description of their physical properties and phase diagrams. This work shows that it is possible to develop such a model but a major theoretical and computational effort will be required. In order to reach this goal, a set of atomic complexes (clustering of atoms) which can describe, simultaneously, the basic structural features of liquids, glasses and solids must be found.

The first step towards such formulation are discussed in this work, based on several inspiring previous works related to hard sphere systems [12-14], metallic glasses [15-18], CVM method [3] and a recently deduced analytical expression for interstitial solutions [10-11]. The methodology presented in this work is based on identification of the energy independent complexes, through careful analysis of the main physical features of the system, and the calculation of their corresponding probabilities. The examples presented in this work show that accurate, general expressions for the configurational entropy of mixing can be developed, even in systems with no translational symmetry.

2. Probabilistic Description of the Configurational Entropy of Mixing

2.1. The Model

The entropy of a classical system with a discrete set of microstates is given by the Gibbs' expression: $S = -k\sum P_i \ln P_i$. The index i labels all the microstates with energy E_i (i=1,…,W) and P_i is the probability of finding a particular configuration of the ensemble consistent with a given energy value. If all microstates are equivalent with the same probability P_i=P=1/W, Boltzmann's expression for the configurational entropy is deduced: *S=-k.ln(P)=k.ln(W).* Thus, the configurational entropy has usually been calculated by computing the number of configurations W. Nevertheless, it was shown that this property can also be deduced by computing probabilities through the inverse problem: *S=-k.ln(P)* [19]. The probability *P* is a conditional one and its analytical determination is usually very difficult. However, if the assumption of energy independent complexes in the mixture is used, the conditional probability can be written as a product of independent probabilities. Therefore, if the complexes in the mixture can be identified, the configurational entropy is written as,

$$S = -k \ln\left(\prod_i \mathrm{p_i}^{n_i}\right) = -k\sum_i n_\mathrm{i} \ln \mathrm{p_i} \tag{1}$$

where n_i and p_i are the numbers and probabilities of each independent complex *i* in the mixture, respectively. Thus, Eq. (1) could be a complement to the traditional method of computing the configurational entropy, helping in the identification and understanding of the representative physical features in complicated systems, such as interstitial solutions or amorphous materials.

One point to comment here is related to the nature of the complexes existing in the mixture: What are those complexes? How should they be selected? The methodology presented in this work shows that a deep understanding of the physical properties of the system is necessary in order to correctly identify the complexes and their changes with composition, temperature and, eventually, lattice distortion. The following section will explain how to select the complex and to deduce an analytical expression for interstitial solutions which can describe SRO, based on the formalism of Eq. (1).

2.1 The Nb-H interstitial solid solution and the selection of the complexes

It was previously mentioned that the source of the difficulties in modeling interstitial solutions arise from the site blocking effects, where the occupation of an interstitial site is prevented by the prior occupation of a neighboring interstitial site. There is an effective repulsion which may be chemical and/or strain in origin. The number of blocked vacancies inhibited for occupancy by other interstitials and, consequently, the size of the blocking sphere, depend on the magnitude of this repulsive interaction.

The first step in modeling any interstitial solid solution is the choice of the number of blocked vacancies associated with each interstitial atom. The resulting structure will be called the ‘basic complex` in this work. In the case of Nb-H system, this selection is mainly related to the length of the H-H interaction. Several models are developed in the literature according to the information selected to deduce them.

Figure 1. The partial configurational entropy of the Nb-H system. Comparison between experimental data and theoretical models available in the literature. The theoretical results are adjusted to the lowest experimental values. The O’Keeffe model [26] displays similar behavior to Boureau’s model [23]. The data for the McLellan model is taken from Ref. [20].

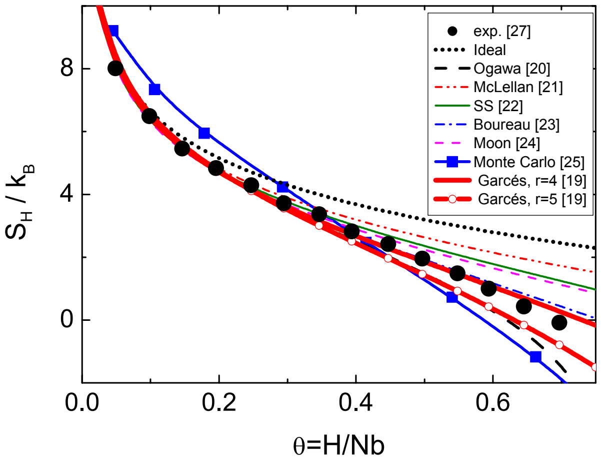


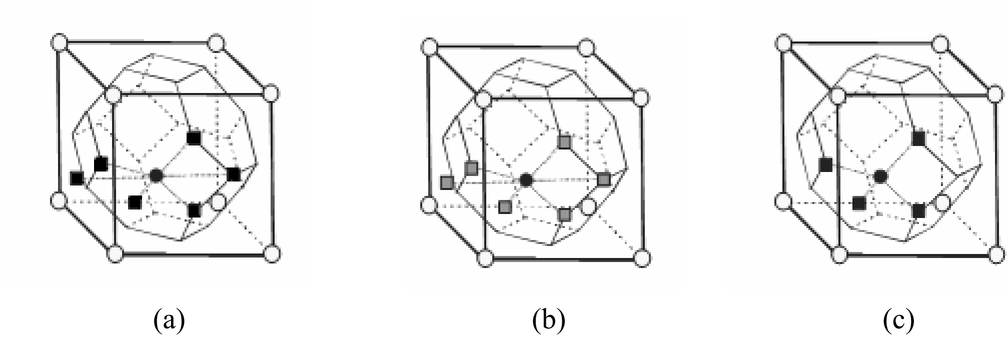
Fig. 1 shows a comparison between the different models for the configurational entropy of mixing available in the literature for Nb-H [19-26] and the experimental data from Veleckis and Edwards [27]. Although all these models are based on the RBM, the best agreement is achieved by the following three models with different approaches to describe the number of vacancies blocked by an interstitial atom:

i)- the Boureau model [23] relies on a hard blocking up to second nearest neighbor, as shown in Fig. 2.a. There are four first-neighbor and two second nearest-neighbor vacancies blocked by one H atom.

ii)- the O’Keeffe model [26] assumes only one interstitial site per metal atom due to the relaxation around a dissolved interstitial atom.

iii)- the model of Ref. [19], by the author of this work, is characterized by a soft blocking of four nearest-neighbor and two second nearest-neighbor sites, shown in Fig. 2.b. There are four first-neighbors and two second-neighbor vacancies blocked by one H atom. Due to the interstitial lattice geometry, only two H atoms can block the same vacancy.

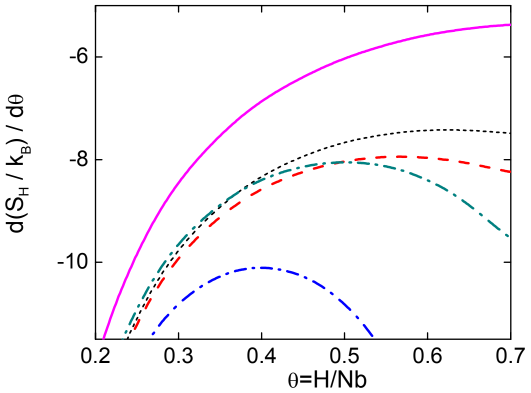
Figure 2. Basic complex or blocking spheres in the Nb-H system for: (**a**) hard blocking of first and second neighbors. (**b**) soft blocking of first and second neighbors. (**c**) hard blocking of first neighbors. Empty circles: Nb host lattice atoms. Full circle: H atom. Dark square: hard blocked vacancies. Grey square: soft blocked vacancies.


(a) (b) (c)

Although the configurational entropy data are well described by the three models, they all give a solubility limit around H/Nb=1.5, in disagreement with the experimental value of H/Nb=1.21±0.04 measured at 750 K [26]. This limit can be described within the model of Fig. 2.c, a hard blocking of first neighbors, but it is incompatible with the experimental data, as shown in Figure 1.

Thus, there are two models for the blocking sphere, represented in Figs. 2.a and 2.b, which correctly describe the configurational entropy data but no the solubility limit, and one model, shown in Fig. 2.c, doing the opposite. What is the solution to the controversy between the solubility limit and the size of the basic complex? At this point, more experimental information should be used. The critical composition of the miscibility gap located at a concentration of H/Nb=θ_c=0.31 in the phase diagram could be helpful in finding an explanation for this inconsistency.

Figure 3. Location of the critical composition of the miscibility gap from different models. Solid line: Speiser and Spretnak. Dot line: Boureau [22] (see Fig. 2.a). Dash line: Garcés [19] (see Fig. 2.b). Dot-dash line: O'Keeffe [26]. Short dash line: Ogawa [19]. None of these models describe the experimental value of θ_c=0.31.



In order to compute the maximum of the miscibility gap through the condition $\left(\partial^2 \Delta G / \partial x^2\right)_{xc} = 0$ [28,29], it is necessary to know the enthalpy of formation ΔH and the free energy G of the solid solution. The calculations of the thermodynamic properties in the cluster field approximation by Vaks and Orlov [30] suggest considerable temperature dependence but an almost linear behavior of the ΔH versus θ in the composition range 0<θ<0.4. Consequently, the extreme condition in this range is due only to an extreme in the configurational entropy since the non-configurational partial molar entropy of mixing of the hydrogen is assumed, as usual, to be independent of temperature and composition [29]. Fig. 3 shows the critical composition predicted by the three most accurate models plotted in Fig. 1. All these models give a critical composition above θ=0.4 adding more confusion to the unexplained physical behavior of H in the Nb-H system. The following question arises again from these results: What is the solution to the controversy between the solubility limit and the length of the H-H interaction, now adding the wrong description of the critical composition of the miscibility gap?

To answer this question it is necessary to develop an adequate theoretical tool which can include SRO and the experimental evidence not taken into account by all previous models. A simple, general analytical expression overcoming the previous cited limitations has recently been deduced [10,11]. The expression, suitable for the treatment of interstitial clustering and SRO, is applicable to tetrahedral or octahedral interstitial solutions in any crystal lattice and for all interstitial concentration. The model for Nb-H developed in Ref. [10] provides the basis for an explanation of unsolved controversies in this system, such as: 1) inconsistencies between the solubility limit and the size of the basic complex, i.e. the size of the blocking sphere, 2) the inaccuracy of the different models for the configurational entropy, 3) the critical composition of the miscibility gap, 4) the length of the H-H interaction, 5) the nature of the α- and α'-phases and 6) the structural relation between the disordered and the ordered phases observed at low temperatures and compositions θ=H/Nb>0.75. In addition, there are several experimental results that can not be explained by the RBM, such as: 1) different experimental [31,32] and theoretical [33,39] results suggest that the H-H interaction is characterized by a repulsive interaction extending out to the third or fourth shell of the interstitial lattice and by an elastic interaction energy outside the radius of repulsion. However, these results contradict the assumptions of the RBM characterized by H-H repulsion up to second nearest neighbors, 2) there is experimental evidence of SRO at very dilute H concentrations (< 1 at.% H) [40]) and in the α'-phase [41,42].

None of these experimental results can be explained by using the RBM or even the CVM methods [39]. This fact shows that the underlying physics of the Nb-H system is still not properly identified and the complexes selected by previous models are not representative of the H behavior. It is clear from a comparison between the models shown in Figures 1 and 3 that the basic source of the controversies related to the Nb-H solid solution is the size of the basic complex and its change with the H concentration.

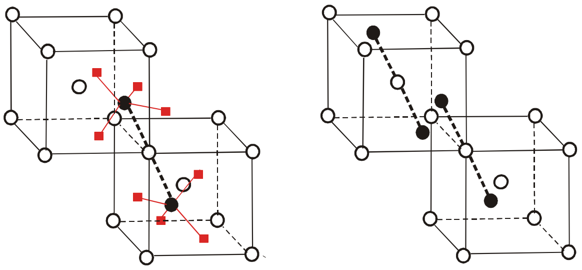
A simple, general expression overcoming the previously cited limitations has recently been deduced [10,11]. The model is based on the following assumptions. Due to interstitial repulsion, the set of vacancies is divided into two different species: n_v^f free vacancies and n_v^b blocked vacancies associated with each interstitial atom. The blocked vacancies do not participate in the mixing process as they are excluded for occupancy by other interstitial atoms. Therefore, it can be assumed that an interstitial complex of size $r_0 = n_v^b + 1$, called basic complex in this work, is formed in the solid solution. It is important to note that interactions between basic complexes can be developed for low temperature or high interstitial concentrations, giving rise to SRO with the formation of new interstitial complexes of size r times the number of interstitial atoms inside them. A small interaction could remain but its magnitude is not enough to create a new kind of complex. Consequently, the complexes are considered in the present model as energy independent entities, i.e. no significant interactions or correlations are assumed between them. Therefore, the original problem could be reinterpreted as a random mixture of independent complexes of different sizes: free vacancies of one lattice site size and n_i interstitial complexes of sizes r_i formed by the interstitial atom and their respective blocked vacancies. The following expression is deduced by applying Eq. 1 [10],

$$\frac{S}{N} = -k\left[\sum_i \theta_i \ln\left(\frac{\theta_i}{\beta - \sum_j \left(r_j - 1\right)\theta_j}\right) + (\beta - \sum_j r_j\theta_j)\ln\left(\frac{\beta - \sum_j r_j\theta_j}{\beta - \sum_j \left(r_j - 1\right)\theta_j}\right)\right] \tag{2}$$

where the indices i and j label all the interstitial complex and free vacancies in the mixture. β is the number of interstitial sites per metal atom, $\theta_i = n_i / N$ is the composition of each independent complex in the solid solution.

How can the controversies previously cited be solved using Eq. 2? The first step is to find the size of the basic complex satisfying the solubility limit, given by β/r_0. The experimental solubility limit of the solid solution, H/Nb=1.21±0.04 [26], can only be described if a basic complex of size $r_0 = 5$ is assumed, see Fig. 2.c, as $\beta=6$ in a bcc lattice. This assumption is incompatible with the experimental data for the configurational entropy, as shown in Fig. 1. However, a combination of basic complexes, arising from SRO, can also describe this limit. The simplest complex fulfilling the previous condition is a pair of H atoms with size $r = 10$, as shown in Fig. 4.a.

Figure 4. Composed objects formed in the solid solutions due to SRO: (a) a pair H-Nb-H with the respective blocked vacancies and (b) a double pair (the blocked vacancies are not shown). Empty circles: Nb host lattice atoms. Full circle: H atom. Squares: blocked vacancies.



(a) (b)

The configurational entropy derived from Eq. (2) for a mixture of vacancies, isolated H atoms and pairs is,

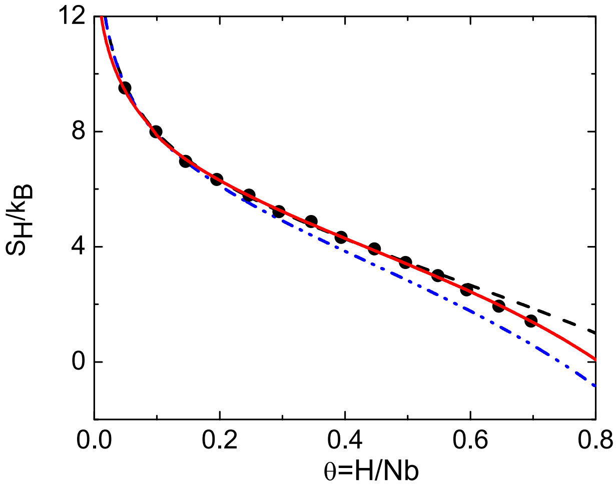
$$-\frac{S}{kN}=\theta_1\ln\left(\frac{\theta_1}{6-4\theta_1-9\theta_2}\right)+\theta_2\ln\left(\frac{\theta_2}{6-4\theta_1-9\theta_2}\right)+(6-5\theta_1-10\theta_2)\ln\left(\frac{6-5\theta_1-10\theta_2}{6-4\theta_1-9\theta_2}\right) \tag{3}$$

In this expression $\beta = 6$ is the number of tetrahedral interstitial sites per metal atom in a bcc lattice, θ_1 is the composition of isolated interstitial atoms and θ_2 the H pair concentration, verifying the relation $\theta_I=\theta_1+2\theta_2$. The growth of pairs has been modeled by the following sigmoid function:

$$\theta=\frac{A}{1+e^{-B(\theta-C)}}\theta_I \tag{4}$$

The parameters are: A=0.10, B=20 and C=0.21. The sigmoid growth with A=0.10 means that an amount of 18% of the H interstitial atoms are located in pairs. The partial configurational entropy is computed numerically and plotted in Fig. 5. The result shows an excellent agreement with the experimental data, giving a critical composition at θ_c=0.33, as Fig. 6 shows. The critical composition of the miscibility gap is not correctly described. Therefore, what is the H physical behavior in this system that it is possible only to explain accurately the configurational entropy?

Figure 5. The partial configurational entropy of Nb-H. Comparison between experimental data and theoretical models presented in this work. Solid line: a random mixture of vacancies, isolated H atoms and pairs with hard blocking of size $r_0 = 5$ and $r = 10$, respectively. Dash line: random mixture of vacancies and random H atoms with hard blocking of size $r_0 = 4$. Dash-dot line: random mixture of vacancies and random H atoms with hard blocking of size $r_0 = 5$.



A major problem in materials science is the description of the critical points. Sophisticated and powerful methods such as CVM fail in these areas due to the huge size of the basic cluster necessary to describe the long-range fluctuations near the critical point. But, what could the description of the current model be if we consider that in the vicinity of the critical point the basic complex changes with the composition? The result of θ_c=0.33, very close to the experimental critical composition, points out the fact that the miscibility gap could be related to an additional structural process, e.g. the clustering or ordering of pairs beginning at a critical composition $\theta_c>0$. The present methodology can be applied easily to modeling of the pair clustering if all the pairs in the mixture are assumed to form double or triple pairs. For this purpose, the same parameters obtained from fitting Eq. (4) to the experimental data are used.

The configurational entropy expression for a mixture of vacancies of size *r=1*, isolated H atoms with size r=5 and double pairs with size *r=20* fulfilling the relation $\theta_I=\theta_1+4\theta_4$ is,

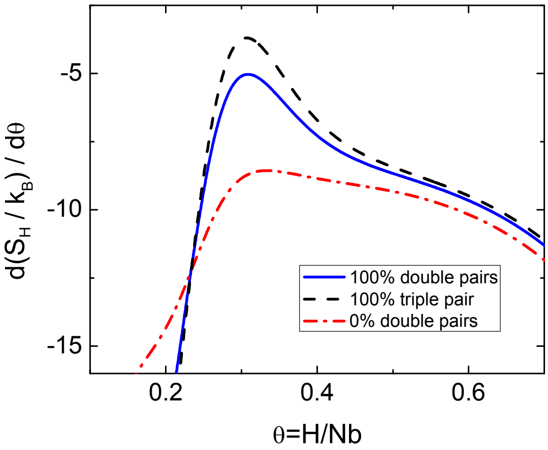
$$-\frac{S}{kN}=\theta_1\ln\left(\frac{\theta_1}{6-4\theta_1-19\theta_4}\right)+\theta_2\ln\left(\frac{\theta_4}{6-4\theta_1-19\theta_4}\right)+\left(6-5\theta_1-20\theta_4\right)\ln\left(\frac{6-5\theta_1-20\theta_4}{6-4\theta_1-19\theta_4}\right) \tag{5}$$

The same expression for triple pairs with size *r=30* fulfilling the relation $\theta_I=\theta_1+6\theta_6$ is,

$$-\frac{S}{kN}=\theta_1\ln\left(\frac{\theta_1}{6-4\theta_1-29\theta_6}\right)+\theta_2\ln\left(\frac{\theta_6}{6-4\theta_1-29\theta_6}\right)+\left(6-5\theta_1-20\theta_4\right)\ln\left(\frac{6-5\theta_1-30\theta_6}{6-4\theta_1-29\theta_6}\right) \tag{6}$$

Fig. 6 shows the location of the partial configurational entropy maximum with the amount of double or triple pairs in the mixture. The model gives a critical composition for the miscibility gap of θ_c=0.307, in remarkable agreement with the experimental value of θ_c= 0.31. This result could resolve the controversies regarding the nature of the disordered phases by characterizing the α'-phase as a random mixture of isolated H atoms and pairs, double and triple pairs.

Figure 6. Location of the critical composition of the miscibility gap with the amount of pair clustering. An extreme is found at θ_c=0.307 if all the pairs are assumed to form double or triple pairs, in remarkable agreement with the experimental value of θ_c=0.31.



The possibility of including SRO in the entropy formalism allows an explanation for several controversies in Nb-H giving a physical picture different to the usual model based on a random mixture of H atoms. The current model makes it possible to solve the contradictions between the length of the H-H interaction and the experimental solubility limit. Moreover, it proposes that the α-phase could be formed by a random mixture of H atoms and H-Nb-H pairs, and the α`-phase is characterized mainly by double or triple pairs in addition to H interstitials. The location of the maximum of the miscibility gap is related to the formation of double or triple pair in the solid solution. It is also proposed in the current model that the double or triple pairs configuration could be interpreted as the seed for the ordered phases observed experimentally for H compositions greater than θ=0.75. The interested reader can find details of the relation between pairs and the ordered phases in Ref. [10].

3. Non-crystalline states of matter

The example of interstitial solutions showed that Eq. (1) provides a useful framework to deduce an analytical expression for the configurational entropy if the basic complex, or basic local structures, vs. H concentration are identified. The liquid and glasses are two particular, very elusive systems due to their lack of periodicity. Is it possible to describe them using the same structural model? There is a great deal of research being carried out in an attempt to answer that question. The results are so abundant that it is almost impossible to encode all the information in an equation. Although it is not the purpose of this work to deduce such an expression, the next sections will analyze the possibilities of finding a common structural model on which to apply the formalism of Eq. (1).

The quantitative description of local structure is a requirement when studying amorphous systems, such as granular matter or glasses. While granular structures are disordered, metallic glasses displays various degrees of structural ordering beyond the short range. This means that a unique ideal structure where all the grain positions are uniquely assigned does not exist. There are a very large number of structures that have equivalent global properties (packing fraction, mechanical properties, etc.) but differ in the way the grains are arranged locally. The identification of the basic motif or structures is fundamental in order to apply the current methodology to compute the configurational entropy. However, how can different forms of disordered configurations with the same energy in systems with no translational symmetry be characterized? The following sections will outline an answer to this question.

3.1 Interacting gas modeling

One of the simplest systems to which the formalism of Eq. (1) can be applied is a gas composed by *n* weak-interacting particles with a finite volume *v* located in a reservoir of volume V. If chemical interaction is strong between them the situation could become not simple. Indeed, new chemical species or atomic complexes could be formed and their identification and counting increase in complexity with increasing density, worsening in the case of liquid and glasses or amorphous materials. If the interaction is small with a magnitude too low to create a new kind of complexes, the probability of finding one particle in a volume V is,

$$p = \frac{nv}{V - nv - \xi} \tag{7}$$

The corresponding entropy from Eq. (1) is,

$$S = -kn \ln\left(\frac{nv}{V - nv - \xi} \right) \tag{8}$$

where ξ(T,V) is a function of the distribution of the non-available holes among the n particles in the volume V. ξ(T,V) is a complicated function to compute for high density gases, liquid or amorphous materials. There are several theories on how to compute it approximately and an enormous number of expressions, theoretically or empirically deduced, for the equation of state (EOS) of this system.

To obtain the EOS from Eq. (8) it is necessary to compute the energy and the energy of the system. The small interaction among the complexes could be assumed, in a simple approximation, to be proportional to the packing fraction *ρ=nv/V*, thus $E \propto nv/V = a/V$. Therefore, the free energy for this simple system is,

$$F = \frac{a}{V} - nkT \ln\left(\frac{nv}{V - nv - \xi} \right) \tag{9}$$

The pressure *P* is,

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,n} = -\frac{a}{V^2} + \frac{nkT}{V - nv - \xi}\left(1 - \frac{\partial \xi}{\partial V} \right) \tag{10}$$

Clearly, the Van der Waals EOS is obtained for this simple model if $nv+\xi = b$ and $\partial \xi / \partial V = 0$. The volume *b* is called excluded volume and is usually assumed to be independent of the density. Rusanov was able to explain the value and meaning of the volume *b* [46-48]. This author proved that the particular constant value *b* = *4v*, assumed in the Van der Waals EOS, corresponds to a linear dependence of the excluded volume on the packing fraction. In any case, to obtain an accurate EOS for all densities it is necessary to know the clustering degree on the fluid density, i.e. *ξ(ρ).* The solution to this problem is still elusive despite countless efforts.

In spite of its simplicity, the Van der Waals EOS gives a qualitative description of the P-V-T behavior of the substances. Eq. (10) shows why the van der Waals model is not appropriate for rigorous quantitative calculations. Indeed, despite the success of some empirical equation with adjustable parameters, Eq. (10) shows the root causes of the inaccuracy and limitations of most EOS available in the literature. They all neglect the term $\partial\xi/\partial V$, an important contribution for high density systems like dense gases and liquids. The advantages of deducing an EOS from Eq. (1) is evident as the approximations used and the limitations are clearly identified.

A different approach to describing the dependence of the excluded volume on the packing fraction, based on an equal-sized hard sphere system, will be presented in the next section.

3.2 Equal-size Hard Sphere System

The hard sphere system is a very simple model for fluids in general. The current scientific literature reports that the equal sized hard sphere system has been used as a model for liquids, crystals, colloidal systems and, in particular, was very successful in modeling granular systems and powders. See Refs. [43-45] and references therein, for reviews in these fields.

An enormous amount of research has been carried out in an attempt to characterize the different basic complexes of disordered configurations in systems with no translational symmetry. Of all these, the results of Aste et al. [12-14] are relevant to this work. These authors found a universal relation fulfilled by all idealized granular materials. The same approach is adopted in this work to find an analytical expression for the configurational entropy of a system composed by equal sized hard spheres.

The model of Aste et al. model is based on a subdivision of the total volume in cells using the Voronoi partition. The authors showed that the local volume distributions of granular packing of monodisperse spherical grains are described very well by a universal distribution function, i.e. k-Gamma distributions. In addition, the volume distribution collapses on the same curve when the data are plotted vs $(v-V_{min})/(<v>-V_{min})$ instead of v. The distribution was deduced using statistical mechanics and a very simple hypothesis that the Voronoi cells in the systems have k degrees of freedom associated with their volumes. k is a structural parameter which depends on the system phase. The main advantage of this model is that the parameter k describes all the crystalline states of the hard sphere system, i.e. from dilute gases to a jammed state. There is a simple dependence of k vs ρ (ρ is the packing fraction) with a sharp transition at the random close packing limit $\rho \rightarrow 0.645$.

The formalism of Section 2 is applied in this work to this idealized system. The identification of the basic complex or motif is fundamental to the application of the current methodology to the computing of the configurational entropy. For this system such structures are the Voronoi cells with k degrees of freedom and volume v. Therefore, the original problem could be reinterpreted as a random mixture of independent complexes of different volumes. We need only to find the number of each complex with a given cell volume and their probability as a function of the total volume V_T. Consequently, in the present approach, only volumetric effects are taken into account.

The volume distribution of the Voronoi cells for a given k is the k-gamma function in the variable v-V_{min}. In this model, the probability p_i of a cell with volume v_i is,

$$p_i = \frac{k^k}{\Gamma(k)} \frac{(v_i - V_{\min})^{(k-1)}}{(\bar{v} - V_{\min})^k} \exp\left(-k \frac{v_i - V_{\min}}{\bar{v} - V_{\min}} \right) \tag{11}$$

The k-gamma function is characterized by a shape parameter k and a scale parameter $(<V>-V_{min})/k$, where V_{min} is the minimum available volume. The total number of complexes is N, equal to the number of hard spheres in the system. The number of each one of the complexes with volume v_i is Np_i. Finally, the expression for the configurational entropy of N hard sphere system is:

$$S = -kN \sum_i p_\mathrm{i} \ln \mathrm{p_i} \tag{12}$$

This expression must be analytically worked in order to get a useful expression to compare with previous expressions and to deduce the equation of state for this idealized system.

3.3 Metallic Glasses

The hard sphere system is a nice example showing the benefit of using Eq. (1) once the physics and the energy independent entities in the mixture are identified. There is another system suitable for application of the same formalism of Eq. (1). This is the bulk metallic glasses (MG) system. Similarly to the interstitial solid solution, the basic complexes change their numbers and structural features with the solvent concentration, and consequently, their probabilities should be computed accordingly. The main task in this system is to compute these quantities while describing, at the same time, the maximum amount of experimental data.

The metallic glasses have at least two different atoms with a significant size difference and have elements with negative heat of mixing, so the structures will try to maximize the number of unlike bonds. The atomic structure of MG is characterized by randomness but it was also shown to have significant SRO and medium-range order (MRO). The origin of both kinds of order has remained unexplained for many years. In addition, MG have exceptionally low volume changes upon fusion, often less than 0.5%, a result firmly established as a property of metallic glasses [18].

Several models have been proposed in the past like the dense random packing (DRP) model due to Bernal [49]. The model is based on monoatomic systems and gives a maximum atom packing fraction about 0.64, too low for modeling real MG. There is other “free volume” model [50], but this does not describe the atomic structures. However, one very insightful method was recently proposed by Miracle to model metallic glasses based on efficient atomic packing [15-18]. The most important feature of this model, called the efficient cluster packing (ECP) model, is that it gives a clue to the atomic structure in function of the composition of the system. Indeed, the main structural properties are described efficiently by the Miracle model.

For the ECP model, the MG consists of clusters characterized by specific identities defined from composition and relative atomic sizes. The basic structure is formed by a dense packing of efficiently packed solute-centered atomic clusters with solvent atoms only in the first coordination shell. The coordination numbers 9, 10, 12, 15 and 17 are the most common and account for almost all binary metallic glasses. The reason behind this behavior remains unexplained. See Fig. 1 of Ref. [17] for details. The MG structure is modeled by placing these characteristic solute-centered clusters on sites of a distorted fcc-like arrangement. Adjacent solute-centered clusters do not overlap and so do not share solvent sites. Solute atoms can occupy any of the four structural site characteristics of the ECP model, but solvent atoms can only occupy sites surrounding the solute atoms. In addition, all solvent sites must be occupied. This model establishes a structural progression of different kinds of clusters according to the solute concentration. ECP is able to predict the minimum glass-forming solute concentration and describe with a small error the density of MG.

In order to apply the formalism of Section 2 to MG, it is necessary to select carefully the basic complex that correctly describes the main physical features mentioned previously. Encoding this information is not easy, and much remains to be done prior to obtaining an analytical expression for the configurational entropy of mixing of MG. The main problem in applying the present formalism to MG systems within the ECP model is to know the distribution of empty space arising from the distorted fcc structure associated with each complex, in a similar fashion to the model of Aste and Coniglio. However, the ECP model is able to describe the density of MG with great precision. Therefore, there should be a way to include the empty space and the work of Aste and Coniglio could be inspiring. This work is under development but more experimental and theoretical information is necessary to advance significantly in this field.

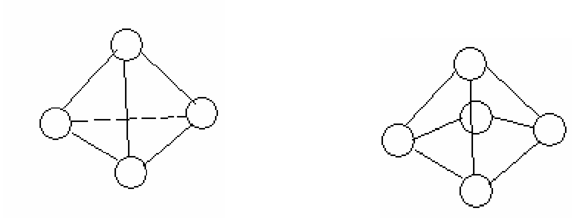
4. Discussion

The examples of Section 3 show that the source of limitations to develop accurate expressions for the configurational entropy in systems with no translational symmetry is the correct treatment of the excluded volume, i.e. the atomic clustering change with the fluid density. Two different approaches to describing this dependence are given in the previous sections: i) the example of weak-interacting gases based on the excluded volume model. The Van der Waals EOS is derived, the approximations used and the limitations are clearly identified and the corrections to improve the accuracy of the EOS is shown, and ii) the Aste and Coniglio model including the empty space, i.e. the associated volume, as a part of the basic complex. Neither approach is easily applicable to systems with more than one component. The clustering degree, chemical or geometrical, and the associated volume should be included in the description. The example of H ordering in Nb-H system offered an alternative to the traditional methodology to describe the clustering of H atoms, i.e. SRO, through the structural changes of the basic complex with composition. Can this formalism be applied to the study of the different states of matter? For this to be possible, a basic complex characteristic of each state of matter must be found. How can it be chosen and how does it change with the density and composition? To answer these questions, the main features of the each state according to the model under current development will be summarized below.

i) Gases: the basic complex should describe the main feature of gases, that is, the high particle mobility in addition to the excluded volume. Eqs. (10) and (12) show two different treatments for the excluded volume. However, these expressions neglect an important contribution, mainly for dense gases and liquids: the influence of the interaction between the particles in the distribution of interstitial holes. In addition, the volume v of each individual particle or molecule should be carefully identified as it could have a associated volume due to internal movement. For example, a gas could have an associated volume as a sphere surrounding it, as usually considered, or it could have an associated volume describing the mean free path.

ii) Liquids: the clustering of particles is essential to any description of this state of the matter. The resulting basic complexes could be individual particles, tetrahedral/pyramids or octahedral clusters, all of which should include the associated volume. The configurational entropy of the liquid state can be computed from Eq. (1) if the structures of the basic complexes in the liquid state are assumed to be individual particles, tetrahedron and pyramid, as shown in Fig. 7.

Figure 7. Possible structures of the liquid state



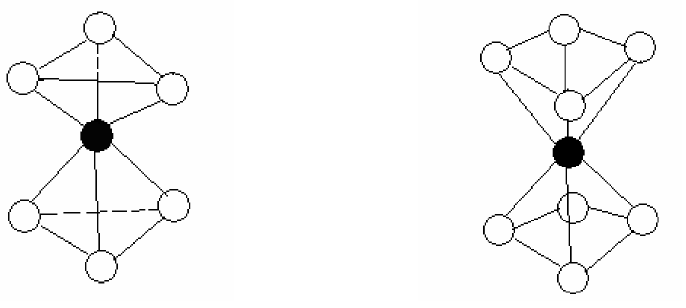
The resulting expression from Eq. (1), as a first approximation to the liquid state is,

$$-\frac{S}{kN} = \theta_1 \ln\left(\frac{\theta_1 v_1}{\theta_1 v_1 + \theta_4 v_4 + \theta_5 v_5}\right) + \theta_4 \ln\left(\frac{\theta_4 v_{41}}{\theta_1 v_1 + \theta_4 v_4 + \theta_5 v_5}\right) + \theta_5 \ln\left(\frac{\theta_5 v_5}{\theta_1 v_1 + \theta_4 v_4 + \theta_5 v_5}\right) \tag{13}$$

θ_1, θ_4 and θ_5 are the composition of each basic complex. The expression should be considered only as a starting point, just for discussion of the possibility of describing the liquid state with the present formalism. In addition, it is applicable to liquids with only one atomic species. For multicomponent liquids, it should be taken into account that the composition of each basic complex is a new independent entity.

It is possible that the geometrical configuration of the basic complexes describing the liquid state changes with density. Two possible structures near the transition liquid-glass/solid are shown in Fig. 9.

Figure 8. Possible connecting structures between liquid state and MG and solids



(a) (b)

The geometrical arrangement schematized in Fig. 9 are common to the structures of MG with coordination numbers 9, 10, 12, 15 and 17, as shown in Fig. 1 of Ref [17]. They are also observed in fcc and bcc structures. While the structure of Fig. 9.a is found along the [111] compact direction in an fcc structure, the structure of Fig. 9.b can be observed along the [001] direction in a bcc structure. In this work, it is proposed that the structure shown in Fig. 9 could be considered as the required connecting structure between the liquid state and the MG and solid state.

iii) Glasses: the ECP model could be a starting point as it gives the changes with composition of the different complex. However, the excluded volume, a priori, should be included in the description. This work is currently under development.

iv) Solids: Inspired by the CVM method, the basic complex shown in Fig. 9 could be used to describe the disordered state. The ordered state in this approach could be described by an association of basic complexes, similarly to the case of H SRO in Nb-H interstitial solution.

To encode all of this information in an equation is no trivial task. Moreover, the enormous amount of experimental and theoretical results makes such development a lengthy process. However, if the attempt is successful and the structures shown in Fig. 9 represent the real connecting basic structure, the desired model that can be applied to all states of matter with the same accuracy and level of description could be achievable.

5. Conclusions

This work presents a formalism to calculate the configurational entropy of mixing alternative to the usual method of counting the number of atomic configurations. The traditional methodology found important restrictions to encode the physical information into compact expressions in complex systems such as interstitial solid solutions or liquids and amorphous materials. The methodology presented in this work is based on the identification of the energy independent complexes in the mixture, through a careful analysis of the main physical features of the system, and the calculation of their corresponding probabilities. The H ordering in Nb-H is used to illustrate the change of the atomic complexes with the H concentration. The possibility of including SRO in the entropy formalism allows an explanation for several controversies in Nb-H giving a physical picture different to the usual model based on a random mixture of H atoms. The current model proposes that the α-phase could be formed by a random mixture of H atoms and H-Nb-H pairs, and the α`-phase is characterized mainly by double or triple pairs in addition to H interstitials. In addition, it explains unsolved controversies in this system related to the length of the H-H interaction, the critical composition of the miscibility gap and the relation between the disordered and the ordered phases.

The methodology is applied to systems with no translational symmetry. It is shown that the source of limitations to develop accurate expressions for the configurational entropy in these systems is the correct treatment of the excluded volume. Three examples are analyzed:

i) a weak-interacting gas. The Van der Waals EOS is deduced and the root causes of the inaccuracy and limitations of this EOS are shown. It neglects an important correction to the repulsive (entropic) term in system with high density, like dense gases and liquids.

ii) non.-interacting equal-size hard sphere system. An expression for the configurational entropy is deduced based on the Aste and Coniglio model for granular systems. This model includes the empty space as associated volume to each hard sphere.

iii) liquids. The clustering of particles is essential to any description of the liquid state. A simple analytical expression for the configurational entropy of the liquid state was computed assuming different clustering degree. The expression should be considered only as an approximation, just for discussing the possibility of describing the liquid state with the present formalism. It is possible that the geometrical configuration of the basic complexes describing the liquid state changes with density. In this case, the expression should be changed accordingly.

If the connecting structures near the transition liquid-glass/solid are identified, a set of atomic complexes changing under densification can be defined. Therefore, the desired model that can be applied to all states of matter with the same accuracy and level of description could be developed.

Conflicts of Interest

The author declares no conflict of interest.

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