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CHEMICALLY CONSTRAINED SYSTEMS: NEW PERSPECTIVES FROM NANOTHERMODYNAMICS.

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ABSTRACT

When describing the thermodynamic properties of multicomponent mixtures, the determination of partial molar quantities like the chemical potential is of great importance for chemical applications. They are used to get a direct access to reaction properties like internal energy , enthalpy, etc. They are also particularly important to describe transport properties like the transport of heat and mass.

By definition, the partial molar quantity, A_i, corresponds to the change in the property A due to a change in the number of particle type i, N_i, when the number of other particle types j, N_j, pressure, P, and temperature, T, are kept constant:

$$A_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,P,N_j}. \tag{1}$$

A_i can then be obtained by a simple derivation of A with N_i under isothermal, isobaric conditions and N_j being constant.

However, when the evolution of one species is coupled to the evolution of other species, what will be called chemical constraints in the following, this last condition can be hardly fulfilled. This is the case for chemical equilibriums like for weak acid base systems where the average concentration of acids and bases are strongly coupled through the value of the acidity constant. This is also and mostly the case for charged systems where electro-neutrality imposes an exact balance between positive and negative charges and so between negatively charged particles and positively charged particles.

Under these conditions it comes directly that A_i characterizes the evolution of A along a path that apparently breaks chemical equilibrium or electro-neutrality, and its determination can then be rather tricky. This does not imply, however, that A_i has no physical meaning. A_i is an intrinsic property of the system. For the extensive property A, we can still write $A = N_iA_i + \sum_j N_jA_j$ and use A_i in thermodynamic relations.

So how can we deal with this condition and obtain A_i when the concentration of each chemical species is not independent on the other species like it occurs in many multicomponent chemical systems (reacting or not) ?

Fluctuations

In order to answer this question it is necessary to adopt a thermodynamic point of view that can fulfill the constraints (electro-neutrality and chemical equilibrium) and the definition of A_i given in Eq. 1 . One solution is to look at open systems or more precisely subsystems embedded in a larger one under equilibrium conditions. The natural ensemble of such small subsystems is the grand-canonical ensemble (GC) where volume, V, temperature and chemical potentials of the different species i, μ_i, are fixed. One can also consider a constant pressure subsystem with fluctuating volume and focus only on situations where the number of particle i fluctuate while the number of the other particle of type j remains constant. For these subsystems, both the conditions of chemical constraints and the equilibrium conditions are fulfilled because they interact with the surrounding. For example the electro-neutrality is not necessarily obeyed in the embedded system but it is strictly satisfied for the whole system, in the grand-canonical ensemble it is also satisfied on average. In consequence it is possible to get access to these partial molar quantities just by looking at open subsystems in interaction with their surroundings [1]. The properties at constant (T,P,N_j) can be determined from the properties obtained in the grand-canonical ensemble (T,V,μ) and thermodynamic relations as described in references [1; 2]. In the following we will mainly focus on properties obtained in the grand canonical ensemble.

From statistical mechanics, we know that, in the grand canonical ensemble, the statistical distribution of the number of each molecular species follows a normal distribution. From this distribution we can directly get the thermodynamic factor, $\Gamma_{ij} = \frac{1}{k_BT}\left(\frac{\partial\mu_j}{\partial \ln N_i}\right)_{T,V,\mu_{k\neq j}}$, from the fluctuation of the number of particle i and j, k_B being the Boltzmann constant :

$$\Gamma^{-1}_{ij} = \frac{\overline{N_iN_j} - \overline{N_i}\,\overline{N_j}}{\overline{N_i}}, \tag{2}$$

where the bar notation indicates an average value. The knowledge of the thermodynamic factor is necessary to relate Onsager transport coefficients, Maxwell Stefan diffusion coefficients and Fick's diffusion coefficients [3]. Γ_{ij} is also related to the Kirkwood-Buff integrals (KBI), $G_{ij} = \frac{V}{N_j}\left(\Gamma_{ij} - \delta_{ij}\right)$, where δ_{ij} is the Kronecker delta function [1; 3; 4]. From KBI, Kirkwood and Buff were able to express the partial molar volume, v_i, for a two component systems, it reads :

$$\overline{v_1} = V\left[\frac{1+(G_{22}-G_{12})N_2}{N_1+N_2+N_1N_2\left(G_{11}+G_{22}-2G_{12}\right)}\right]. \tag{3}$$

As describe in ref. [2], the partial molar internal energy and enthalpy can also be determined from the fluctuations of internal energy, U, in the grand canonical subsystems :

$$\left(\frac{\partial \overline{U}}{\partial \overline{N_i}}\right)_{T,V,\mu_{j\neq i}} = \frac{\overline{UN_i} - \overline{U}\,\overline{N_i}}{\overline{N_i^2} - \overline{N_i}^2}, \tag{4}$$

$$\left(\frac{\partial \overline{H}}{\partial \overline{N_i}}\right)_{T,V,\mu_{j\neq i}} = \left(\frac{\partial \overline{U}}{\partial \overline{N_i}}\right)_{T,V,\mu_{j\neq i}} + \frac{k_B T}{\Gamma_{ii}}. \tag{5}$$

As previously indicated the transformation of the partial molar derivatives from (T,V,μ_j) to (T,P,N_j) conditions can be done with the help of thermodynamic relations [1; 2].

Size dependence

Partial molar quantities has been recently computed from molecular simulations, Monte-Carlo (MC) and molecular dynamics (MD), looking at fluctuations in embedded subsystems for atomic and molecular fluid systems (reactive or not). It has been shown that when the embedded systems are small, the calculated KBI or partial energy varies like $1/L$ where L is a characteristic length of the subsystem [2; 5; 6; 7; 8; 9]. The thermodynamic limit of the properties are then obtained by linear extrapolation of the fluctuation results from different L sizes. This is illustrated on Figure 1 for a ternary system, composed of three components called A, B and W, with the constraint that the mole fraction of A and B are identical ($x_A = x_B$). The particles interact through the soft repulsive potential Weak Chandler Andersen (WCA) with the same diameter, σ, but different energy parameters. Here we used spherical subsystems having different radius sizes, R. The KB integrals vary linearly like $1/R$ and the extrapolation for $R = \infty$ gives results in agreement with data obtained from grand canonical Monte-Carlo simulations (GCMC). Here the use of GCMC as a reference is justified because the particles interact through weak short range potential. This would not have been the case for charged particles with electrostatic interactions.

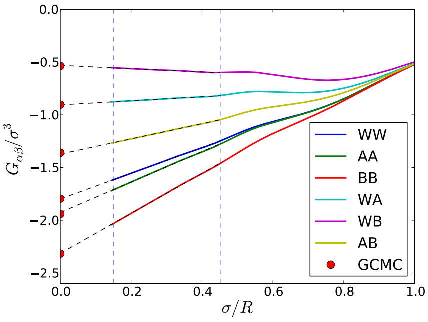

Figure 1: KB integrals $G_{\alpha\beta}(R)$ as a function of σ/R for the ternary WCA system W, A, B ($x_A = x_B = 0.25$) as computed from MD simulations in the canonical (NVT) ensemble.

This size dependence can be understood as an effect of smallness of the subsystems. The size of individual particles is not infinitely small comparing to the size of the subsystems, so the number of particles located at the surface cannot be negligible compared to the total number of particles located in the subsystems. The consequence is that surface effects take place and explain this behavior in $1/L$ [7; 9].

In order to deal with the size dependance of thermodynamic properties it is possible to use the Gibbs surface thermodynamics to treat these systems where surface effects are important. More recently, in the sixties, T.H. Hill extended classical thermodynamics in a way that provides a thermodynamically coherent description from small systems to the thermodynamic limit [10]. It is called the thermodynamics of small systems or nanothermodynamics when applied to nanoscale systems. As we have shown, this approach gives a theoretical basis to treat such small embedded system and it is coherent with the approach of Gibbs to treat surfaces [9]. On Figure 1, the values of G_{ij} change with size, although we mainly extrapolate G_{ij} at infinite sizes where classical thermodynamics is valid we could have applied the thermodynamics of small systems before reaching the limit. This method which consists of getting properties at the thermodynamic limit from extrapolation for different size is called small system method (SSM).

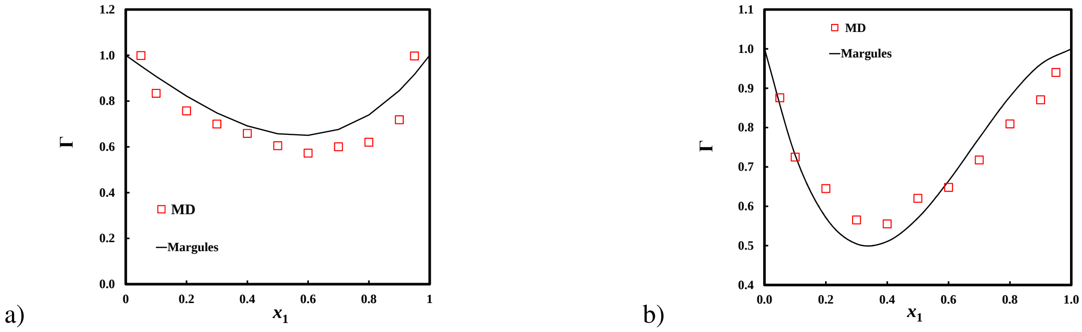

Figure 2: Thermodynamic factor Γ_{12} in the binary systems a) acetone (1)methanol (2) and b) acetone (1) tetrachloromethane (2) at 298 K, 1 atm [3]. Open symbols are the computed Γ using MD simulations. The solid lines represent Γ calculated from the Margules model fitted to experimental vapor-liquid equilibrium data.

Results

The Γ_{12} values of not-constrained molecular systems were computed from molecular dynamics simulations by applying the SSM method [3]. They are plotted on Fig. 2, they are in excellent agreement with experimental results.They show a large deviation from the value unity which is the sign of non-ideality.

In another work the reaction H_2=2H was simulated by using a reactive force field. The partial molar enthalpies, H_i, of the different species i were computed from molecular dynamics simulations at different temperatures and density conditions [11]. The reaction enthalpies were calculated from the values of H_i and plotted as a function of the temperature on Fig. 3. For this chemically constrained system we could calculate the "ideal" equilibrium constants from the mole fractions (instead of the chemical activities) and extract the "ideal" reaction enthalpies with the van't Hoff equation. The results show a large deviation between the ideal and the non-ideal results which are much closer to the expected experimental results.

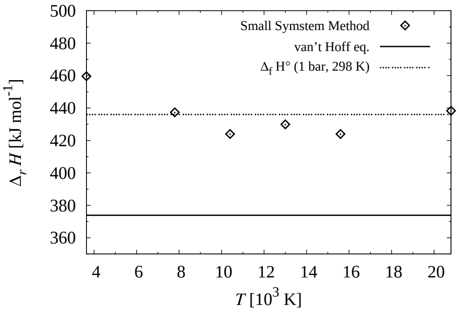

Figure 3: Reaction enthalpy of the reaction H_2=2H at different temperatures calculated from the small system method [11]. The values are compared with ideal results obtained from van't Hoff equation and with the experimental heat of formation.

When using long range potential, like the coulomb potential, the effect of the presence of additional charges in a system can change a lot its physics, as mentioned above. To avoid such problem we computed partial molar quantities from the KB integrals, see Eq. 3, and the SSM on NaCl diluted in water. The system is electro neutral. From the simulations we could obtain the partial molar volume. At 350 K we find for water V_W = 0.0308 nm^3/molecule, V_{Na^+} = -0.0325 nm^3/molecule and V_{Cl^-} = 0.0754 nm^3/molecule. The molar volume of NaCl V_{NaCl}= V_{Na^+}+V_{Cl^-}=0.0429 nm^3/molecule which is in good agreement with experiments V_{NaCl}=0.0416 nm^3/molecule and V_W = 0.0292 nm^3/molecule. The possibility to have access to individual ionic partial molar quantities is particularly important to determined the thermodynamic properties of electrolytes.

These results show that the small system method applied to grand canonical subsystems is well adapted to have access to partial molar quantities even for chemically constrained systems.

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