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The one dimensional binary fluid

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Abstract. In this paper we find the equation of state for a one dimensional binary fluid through an analysis that involves the use of the Partition Function, the Gran Partition Function and Generalized Ensemble. The binary fluid treated here has some intrinsic interest, firstly because we will apprroach the continuum by means of a lattice variable, and secondly, because we assume the interaction between nearest neighbor particles to be arbitrary.

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1. Introduction

In this paper we generalize the method used by Poland and Scheraga [1] to solve a one dimensional fluid lattice model, for the case in which two different types of particles (A or B) are assumed, *i.e.* for a one dimensional binary fluid. Furthermore we will prove in a straightforward form that the solution of the Generalized Ensemble leads to obtain the Kikuchi [2] equation of state, if we let the lattice variable $\delta \to 0$. However, since the result obtained through this analysis is valid for any *shape* of the pair potential between nearest neighbor particles we will also prove that the solution includes as a particular case the lattice model of regular solutions discussed by Guggenheim [3]. Moreover, using the analytic result obtained in this analysis we will find an analytic expression for the free energy change of the mixture.

Finally, if we consider the binary fluid mixture as a Markoff chain, we will find an analytic expression for the conditional probability that, given a particle (A or B), will be followed by a specified particle (A or B) independent from the number of unoccupied sites between them.

We think that the analysis developed in this paper can be useful for physicists for three reasons. First of all, because it provides an alternative point of view to obtain classical results in Statistical Mechanics, such as the Kikuchi equation of state. Second, because this kind of analysis might lead to a good workable model for the study of more complex systems in one dimension for example, when we assume that there are many types of particles; *i.e.* for a one dimensional multicomponent mixture. And third, because the following analysis is an unusual application of the Generalized Ensemble, which permits us to derive many analytic relations of physical interest.

The outline of the paper is as follows. The binary mixture model is introduced and solved in section 2. The equilibrium constant obtained in the *quasi-chemical* approximation, as well as the analytic expression for the conditional probability (for the case in which we consider the chain as Markovian) are derived in section 3.

2. The binary mixture model

In the following we assume that the reader knows the work of Poland and Scheraga [1], so we omit the discussion of the many aspects related to the lattice model. As in the one dimensional lattice fluid [1], we consider that each particle of the mixture is assigned the constant interatomic potential $\phi(n)$ over the interatomic distance $r_0\delta(n-1/2)$ to $r_0\delta(n+1/2)$. For the case in which we let $\delta \to 0$, $\phi(n)$ approaches the smooth function $\phi(r)$. Moreover, in this model we assume that the interaction potential between nearest neighbor particles is arbitrary, and we take the potential as

$$\phi(r) = \begin{cases} \infty & \text{for } r \leq r_0, \\ \phi(r) & \text{for } r_0 \leq r < 2r_0, \\ 0 & \text{for } r \geq 2r_0, \end{cases} \tag{1}$$

or since $r = nr_0\delta$ for n lattice sites $\phi(r) = 0$ for $n \geq n_0 = 2/\delta$.

Furthermore, a Boltzman factor q_n^{AA} is assigned to a pair of particles separated by n lattice sites

$$q_n^{AA} = e^{-\beta\phi(nr_0\delta)}, \tag{2}$$

where $\beta = (k_B T)^{-1}$, k_B denotes the Boltzman constant, and T the absolute temperature. There is, of course, a similar equation for a pair BB or AA. Then, taking into account equation (1) the Boltzman factor will satisfy

$$q_n^{AB} = q_n^{AA} = q_n^{BB} = 1, \qquad \text{for} \quad n \geq 2/\delta. \tag{3}$$

On the above assumption, it is easy to see the binary mixture as a series of succesive independent sequences of particle A or B and a run of holes (because of the cut-off of the potential at $2r_0$). For example, for one possible distribution of A and B particles, we can see the lattice as

$$\cdots \underbrace{A\,0\,0\,0\,0}_{q_5^{AB}} \quad \underbrace{B\,0\,0\,0}_{q_4^{AB}} \quad \underbrace{A\,0\,0}_{q_3^{AB}} \quad \underbrace{B\,0\,0}_{q_3^{BB}} \quad B\cdots, \tag{4}$$

where A stands for a particle A (*idem* for B) and 0 for a hole. The contribution of the sequence given in the above distribution to the Partition Function would be $q_5^{AB} q_4^{AB} \cdots$. Each sequence contains a particle A or B, and is assigned a factor Δ^{-1} from the momentum integration. In the following we assume that this factor Δ^{-1} is absorbed in the Boltzman factors. Then it is not difficult to see that the Partition Function is given by

$$Z(N,M) = \sum_{N_{AB}} \sum_{n_\sigma^{AA}} \prod_{\sigma=1}^{N_{AA}} q_{n_\sigma}^{AA} \sum_{n_\sigma^{BB}} \prod_{\sigma=1}^{N_{BB}} q_{n_\sigma}^{BB} \sum_{n_\sigma^{AB}} \prod_{\sigma=1}^{N_{AB}} q_{n_\sigma}^{AB}, \tag{5}$$

where σ is an index designating the number of sequences. In equation (5) there are two constraints

$$\sum_{\sigma=1}^{N_{AA}} n_\sigma^{AA} + \sum_{\sigma=1}^{N_{AB}} n_\sigma^{AB} + \sum_{\sigma=1}^{N_{BB}} n_\sigma^{BB} = M, \tag{6}$$

where M represents the number of sites, and

$$N = \text{constant}, \tag{7}$$

where N represents the number of particles.

It is important to take into account that the following relation between (N_A, N_B) and (N_{AA}, N_{AB}, N_{BB}) will be useful [6]

$$\begin{aligned} N &= N_A + N_B, \\ 2N_A &= 2N_{AA} + N_{AB}, \\ 2(N - N_A) &= 2N_{BB} + N_{AB}, \end{aligned} \tag{8}$$

where N_A and N_B represent the number of particles of A and B type, and N_{AA}, N_{BB} or N_{AB}, represent the number of pair AA, BB or AB particles.

Under the above constraints, we know no easier way to evaluate the Partition Function explicitly. However, the Gran Partition Function is given by

$$\Xi = \sum_{N=0}^{M} Z(N,M)Y^N \tag{9}$$

with only one constraint (given by equation (6)).

If we continue with this procedure [1], we find that the Generalized Ensemble is given by

$$\gamma = \sum_{M=0}^{\infty}\sum_{N=0}^{M} Z(N,M)Y^N X^{-M}, \tag{10}$$

where all the constraints have been removed and where $X = e^{\beta p \delta}$.

In the above expression, if we take into account both [1]

$$\sum_{M=0}^{\infty}\sum_{N=0}^{M} = \sum_{N=0}^{\infty}, \tag{11}$$

and the following relation

$$X^{-M} = \prod_{\sigma=1}^{N_{AA}} X^{-n_\sigma^{AA}} \prod_{\sigma=1}^{N_{BB}} X^{-n_\sigma^{BB}} \prod_{\sigma=1}^{N_{AB}} X^{-n_\sigma^{AB}}, \tag{12}$$

we can write the Generalized Ensemble as

$$\gamma = \sum_{N=0}^{\infty}\sum_{N_{AB}} C_N \Big(\sum_{n=1}^{\infty} q_n^{AA} X^{-n}\Big)^{N_{AA}} \Big(\sum_{n=1}^{\infty} q_n^{AB} X^{-n}\Big)^{N_{AB}} \Big(\sum_{n=1}^{\infty} q_n^{BB} X^{-n}\Big)^{N_{BB}} Y^N. \tag{13}$$

The factor C_N appears when we eliminate the constraint over the order of sequence, and is givey by

$$C_N = \frac{N_A!(N-N_A)!}{(N_{AB}/2)!^2(N_A - N_{AB}/2)!(N - N_A - N_{AB}/2)!}. \tag{14}$$

The exponents of the parenthesis in equation (13) represent the molar fractions of particles for each species (A or B), and can be modified using equation (8) and the following relations:

$$\theta = N_A/N \quad \text{and} \quad (1-\theta) = (N - N_A)/N, \tag{15}$$

obtaining

$$\gamma = \sum_{N=0}^{\infty} \sum_{N_{AB}} C_N \Big(\sum_{n=1}^{\infty} q_n^{AA} X^{-n} \Big)^{N^*_{AA}} \Big(\sum_{n=1}^{\infty} q_n^{AB} X^{-n} \Big)^{N_{AB}} \Big(\sum_{n=1}^{\infty} q_n^{BB} X^{-n} \Big)^{N^*_{BB}} Y^N, \tag{16}$$

where

$$N^*_{AA} = (\theta - N_{AB}/2N) \quad \text{and} \quad N^*_{BB} = (1 - \theta - N_{AB}/2N),$$

In order to evaluate the double sum in equation (16) we are going to maximize the second sum, respect to N_{AB} and then we are going to sum over N. The condition for finding out the maximum is given by

$$\partial \ln \xi(N', N_{AB})/\partial N_{AB} = 0, \tag{17}$$

where $\xi(N', N_{AB})$ is any term of the Generealized Ensemble and is given by

$$\begin{aligned} \xi(N', N_{AB}) = C'_N \Big(\sum_n q_n^{AA} X^{-n} \Big)^{N'(\theta-\alpha)} \\ \times \Big(\sum_n q_n^{BB} X^{-n} \Big)^{N'(1-\theta-\alpha)} \Big(\sum_n q_n^{AB} X^{-n} \Big)^{2N'\alpha}, \end{aligned} \tag{18}$$

with

$$\alpha = N_{AA}/2N', \qquad \theta = N_A/N' \quad \text{and} \quad (1 - \theta) = N' - N_A/N, \tag{19}$$

Then, with (17) in (16) we find:

$$\frac{\partial \ln C'_N}{\partial N_{AB}} = \ln \left\{ \frac{\left(\sum_n q_n^{AA} X^{-n} \right) \left(\sum_n q_n^{BB} X^{-n} \right)}{\left(\sum_n q_n^{AB} X^{-n} \right)} \right\}^{1/2}. \tag{20}$$

Using the Stirling approximation we can find in a straighforward way the next equality

$$\frac{\partial \ln C'_N}{\partial N_{AB}} = \ln \left\{ \frac{\left(\theta - \alpha \right)^{1/2} (1 - \theta - \alpha)^{1/2}}{\alpha} \right\}. \tag{21}$$

From equations (20) and (21) the following relation is found

$$\frac{(\theta-\alpha)(1-\theta-\alpha)}{\alpha^2}=\frac{\left(\sum_n q_n^{AA}X^{-n}\right)\left(\sum_n q_n^{BB}X^{-n}\right)}{\left(\sum_n q_n^{AB}X^{-n}\right)}. \tag{22}$$

On the other hand [1,5] for undistinguishable particles the following relation is valid

$$Y\sum_{n=1}^{\infty} q_n X^{-n}=1. \tag{23}$$

Then we can say, without loosing generality, that the next relation is valid too

$$Y_{AA}\sum_{n=1}^{\infty} q_n^{AA}X^{-n}=1. \tag{24}$$

The above equation represents an analytic relation between the activity (Y), the intereaction potential (ϕ) and the pressure (p) for one system with A particles only. Then, taking into account that $Y_{AA}=e^{\beta\mu_{AA}}$ we can write equation (24) as follows

$$e^{-\beta\mu_{AA}}=\sum_{n=1}^{\infty} q_n^{AA}X^{-n}, \tag{25}$$

where μ_{AA} represents the chemical potential for the A species. If we put equation (25) in (22) we find

$$\frac{(\theta-\alpha)(1-\theta-\alpha)}{\alpha^2}=e^{2\mu_{AB}-\mu_{BB}-\mu_{AA}}=e^{\beta\omega}, \tag{26}$$

which gives a cuadratic relation for $\alpha(N_{AB})$. If we solve this, we find the value of N_{AB}^{*} which maximized the second sum in equation (16). We pause here to consider the meaning of equation (26). Through this equation we can see that if ω is negative, the pairs (AA) and (BB) are more stable than (AB). On the other hand, if ω is positive, the pair (AB) is more stable than (AA) or (BB) pairs and if ω is zero, the distribution of the pairs is random. We can understand this more easily, if we view the term $e^{\beta\omega}$ in equation (26) as the equilibrium constant (associated with the molar free energy change) or the reaction

$$2(AB)\rightleftarrows(AA)+(BB). \tag{27}$$

Returning to the evaluation of γ, if we solve equation (26) for α, we find

$$\alpha = \frac{2\theta(1-\theta)}{\epsilon+1} \quad \text{and} \quad \epsilon = [1-4\theta(1-\theta)(1-e^{\beta\omega})]^{1/2}. \tag{28}$$

Using the above relation we can write for the Generalized Ensemble the following expression

$$\gamma = \sum_{N=0}^{\infty} C_N \left\{ \left(\sum_{n=1}^{\infty} q_n^{AA} X^{-n} \right)^{\hat{\theta}} \left(\sum_{n=1}^{\infty} q_n^{AB} X^{-n} \right)^{\theta'} \left(\sum_{n=1}^{\infty} q_n^{BB} X^{-n} \right)^{\alpha'} \right\}^N Y^N, \tag{29}$$

with $\hat{\theta} = \theta - \alpha$, $\theta' = 1 - \theta - \alpha$, $\alpha' = 2\alpha$ and

$$C_N = \frac{(N\theta)!(N(1-\theta))!}{(N\alpha)!^2(N(\theta-\alpha))!(N(1-\theta-\alpha))!}. \tag{30}$$

If we apply Stirling approximation to equation (30) we can rewrite equation (29) in such a way that the following relation is easily found [5] (after taking into account that $\gamma^{-1} = 0$):

$$Y = \left[\frac{\theta^{\theta}(1-\theta)^{1-\theta} \left(\sum_{n=1}^{\infty} q_n^{AA} X^{-n} \right)^{\hat{\theta}} \left(\sum_{n=1}^{\infty} q_n^{AB} X^{-n} \right)^{\theta'} \left(\sum_{n=1}^{\infty} q_n^{BB} X^{-n} \right)^{\alpha'}}{\alpha^{2\alpha}(\theta-\alpha)^{\theta-\alpha}(1-\theta-\alpha)^{1-\theta-\alpha}} \right]. \tag{31}$$

Using this relation we can find the equation of state in a straightforward form, if we compute

$$\rho = \delta^{-1}(\partial \ln Y / \partial \ln X)^{-1} \tag{32}$$

for the density ρ. Taking into account that $\alpha = 2\theta(1-\theta)/(\epsilon+1)$ wen can rewrite equation (31) as

$$\ln Y = -\ln(\epsilon+1) + \theta\{\ln(\epsilon-1+2\theta) + \beta\mu_{AA}\} + (1-\theta)\{\ln(\epsilon+1-2\theta) + \beta\mu_{BB}\}. \tag{33}$$

Then the equation of state is given by

$$\rho = \left\{ \frac{\partial}{\partial \beta p} \Big[\ln(\epsilon+1) - \theta\{\ln(\epsilon-1+2\theta) + \beta\mu_{AA}\} - (1-\theta)\{\ln(\epsilon+1-2\theta) + \beta\mu_{BB}\} \Big] \right\}^{-1}. \tag{34}$$

The above expression represents the well known Kikuchi equation of state [2] for a one dimensional binary fluid. It is important to mention that in the earlier procedure we said nothing with respect to the value of the lattice variable δ. In particular, if we want to obtain the solution for a continuum fluid the following relation substitutes equation (24) for the chemical potential

$$\lim_{\delta \to 0} e^{-\beta \mu_{ij}} = \int_0^\infty e^{-\beta(\phi_{ij}(r)+pr)}\, dr, \tag{35}$$

Furthermore, one thermodynamic parameter that we can compute using equation (33) is the free energy change for the mixture. As it is known, the following relation is valid

$$e^{-\beta G/N} = e^{-\beta \mu}, \tag{36}$$

where G represents the Gibbs free energy for the mixture and μ the chemical potential. Using equation (36) we obtain the following expression for the free energy change of the mixture

$$\begin{aligned} \beta \Delta_m G/N &= \beta(G - \theta G_{AA} - (1-\theta)G_{BB})/N \\ &= \theta \ln(\epsilon - 1 + 2\theta) + (1-\theta)\ln(\epsilon + 1 - 2\theta) - \ln(\epsilon + 1) \end{aligned} \tag{37}$$

where G_{AA} and G_{BB} represent the Gibbs free energy for the pure species A and B respectively.

3. A particular case: the lattice regular solution

As we mentioned in the introduction, the result obtained in the above analysis is independent from the *shape* of the pair potential interaction. Then we will be able to obtain the results for the lattice regular solutions, as we can see in what follows. The Bragg-Williams [6] theory assumes that the distribution of particles is *random* in a binary solution. This assumption is not true in general, because if the forces between (AA), (BB) or (AB) particles are not the same, the order in the lattice is more favorable for certain sequences than for others. Naturally, this effect will be small for high temperature, because the thermic agitation breaks any order. On the other hand, Guggenheim [3] proposes an approach to take into account that the distributions of the pairs AA, BB or AB are not the same. He assumes that the value of N_{AB}, can be obtained from the following equilibrium processes

$$2(AB) \rightleftarrows (AA) + (BB). \tag{38}$$

This procedure is analogous to a chemical reaction, and Guggenheim refered to it as a *quasi-chemical* equilibrium. In our model the conditions given in the *quasi-chemical* approximation, which in one dimension is exact, are given by

1) $\delta = 1$, this means, any particle occupies only one site

2) $N_A + N_B = M$, this means, each site is occupied by only one particle.

Under this conditions, the Boltzman factors, defined in equation (2), are given by

$$q_{AA} = e^{-\beta\epsilon_{AA}}, \qquad q_{BB} = e^{-\beta\epsilon_{BB}} \quad \text{and} \quad q_{BA} = e^{-\beta\epsilon_{AB}}, \tag{39}$$

where ϵ_{AA} represents the interaction energy between AA pair (*idem* for BB and AB). In this case ω, as defined in equation (26) is given by

$$\omega = \epsilon_{AB} - \epsilon_{AA}/2 - \epsilon_{BB}/2 = \Delta\epsilon/2, \tag{40}$$

then the equilibrium constant for the reaction given in equation (38) is given by

$$e^{-\beta\Delta\epsilon} \tag{41}$$

which is the same that we would obtain through the *quasi-chemical* approximation.

Another information of interest that can be computed related to the conditional probability $P_{A/A}$, which represents the probability that given any particle A, it will be followed by another particle A, independent from the number of unoccupied sites between them.

To obtain one analytic expression for $P_{A/A}$ we defined this as

$$P_{A/A} = F_{AA}/F_A, \tag{42}$$

then taking into account that

$$F_{AA} = N_{AA}/N \quad \text{and} \quad F_A = N_A/N, \tag{43}$$

with

$$2N_A = 2N_{AA} + N_{AB} \quad \text{and} \quad \theta - \alpha = N_{AA}/N, \tag{44}$$

we can write equation (42) for $P_{A/A}$ as

$$P_{A/A} = \theta - \alpha/\theta. \tag{45}$$

Let us remember that the parameter α is defined as

$$\alpha = 2\theta(1-\theta)/(\epsilon+1)$$

then the conditional probability $P_{A/A}$ is given by the following expression

$$P_{A/A} = \epsilon - 1 + 2\theta/(\epsilon + 1). \tag{46}$$

It is not difficult to obtain a similar expression for $P_{B/B}$ and $P_{A/B}$. Now, if we considere the binary mixture as a Markoff chain, the probability to find the following sequence

$$\cdots AAAAABBAABBBBBAAAABAA\cdots$$

is given by

$$\cdots (P_{A/A})^9 (P_{A/B})^6 (P_{B/B})^6. \tag{47}$$

It is important to mention that in the above analysis we have omited the thermodynamic discussion of the one dimensional mixture or of the regular solutions, because the reader can find this in the original paper by Kikuchi [2] or Guggenheim [3].

In this paper we analized the one dimensional binary fluid model, but the method discussed can be entirely extended to any number of components. In this case it is possible to derive the result obtained by Longuet Higgins [4] for a one dimensional multicomponent mixture.

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Resumen. En este trabajo nosotros encontramos la ecuación de estado de un fluido binario unidimensional a través de un análisis que involucra el uso de la Función de partición, la Gran función de partición y el Conjunto generalizado. El fluido binario tratado aquí tiene un interés particular, primero porque aproxima el continuo por medio de una variable de red y segundo porque supone que la interacción entre vecinos cercanos es arbitraria.