A lattice model of hydrogen bonding in mixtures. I. General formulation in terms of weak

subgraphs

A lattice model of hydrogen bonding in mixtures:
I. General formulation in terms of weak subgraphs

A Bellemans, J-P Ryckaert and D Beltus

Department of Physics, CP 223, Université libre de Bruxelles, 1050 Brussels, Belgium

Abstract. A particular version of the lattice model of Abraham and Heilmann for hydrogen-bonded systems is worked out by means of a weak subgraph expansion. Each site may be occupied by one molecule, A or B, and two neighbouring molecules A may bind together, as far as neither of them is already engaged in more than one bond. It turns out that, for a wide range of the parameters involved in the model, the zeroth approximation (replacement of the true lattice by a Bethe lattice) leads to reasonable values of its thermodynamic properties.

1. Introduction

Some kinds of molecules, typically alcohols, are able to associate rather strongly by forming hydrogen bridges. As a consequence, the mixture of an alcohol A (like ethanol) with an inert solvent B (such as tetrachloromethane) is usually regarded as a multicomponent system of monomers A and B, plus a whole variety of dimers, trimers, ... n-mers, ... of molecules A. The thermodynamic properties of such mixtures have been usually formulated by introducing a set of association constants K_n, one for each kind of n-mer, various assumptions being subsequently made (i) on the mixing properties of the different molecular species (ideal or non-ideal mixing) and (ii) on how these various K_n are interrelated (Prigogine *et al* 1956).

An alternative to these 'chemical' theories was presented a few years ago by Abraham and Heilmann (1972, 1975) who introduced a new type of two-component lattice model, applying precisely to the case considered here: each site is occupied by one molecule, A or B, and the A molecules are able to form bonds with neighbouring ones of the same species, up to a maximum number p, each bond formation reducing the free energy of the system by a definite amount. Abraham and Heilmann were however essentially interested in the existence of order–disorder transitions in their model, in relation to p, and not in its detailed thermodynamic properties. Here our aim will precisely be to evaluate these properties explicitly for the particular case $p = 2$, i.e. each A is allowed to bind at most two times. This model which displays no phase transition, corresponds reasonably well to the mixture of an alcohol with an inert solvent; it allows the formation of cyclic as well as open chains of A molecules, the determining factors being (i) the free energy of formation of the bonds and (ii) the lattice structure (mainly through its coordination number q).

This model will be treated by a method originally developed by Nagle for the ice problem (Nagle 1966a) and the monomer–dimer problem (Nagle 1966b), in such a way that the logarithm of the grand partition function (and all subsequently derived

quantities) eventually separates into two terms, the first one in a close analytic form and the second one as an expansion in correspondence with a class of weak subgraphs associated to the lattice. It will be shown that, for situations of practical interest, the first term is largely dominant.

2. Formal treatment of the grand partition function

Consider a homogeneous lattice of V equivalent sites, with coordination number q, each site being occupied either by a molecule A ('alcohol') or by a molecule B ('inert solvent'), with the following rule:

> 'Two neighbouring molecules A are allowed (but not compelled) to form a bond, provided that neither of them is already engaged in more than one bond'.

Given the numbers N_0, N_1 and N_2 of A molecules respectively engaged into 0, 1 or 2 bonds (denoted hereafter as A_0, A_1 and A_2), the grand partition function of the system reads

$$\Omega = \sum_{N_1} \sum_{N_2} (z_A + z_B)^{V - N_1 - N_2} (z_A y_1)^{N_1} (z_A y_2)^{N_2} h(N_1, N_2)$$

$$= (z_A + z_B)^V \sum_{N_1} \sum_{N_2} (z y_1)^{N_1} (z y_2)^{N_2} h(N_1, N_2); \tag{2.1}$$

z_A, z_B are the activities, z is defined as

$$z = z_A / (z_A + z_B), \tag{2.2}$$

$h(N_1, N_2)$ is the number of different bond arrangements and y_1, y_2 are Boltzmann weights associated with A_1 and A_2 respectively, so that bonds A_1-A_1, A_1-A_2 and A_2-A_2 contribute as y_1^2, $y_1 y_2^{1/2}$ and y_2. (Should all bonds be equivalent, then $y_2 = y_1^2$; the introduction of two weights y_1, y_2 makes the model more flexible: for $y_2 = 0$, molecules A can only dimerise while for $y_1 = 0$, they can only polymerise in cycles.)

Let us number all sites $1, \ldots i, \ldots V$ and denote their occupancy by a set of variables $s_1, \ldots s_i, \ldots s_V$. Each site may be occupied by either A_2, A_1 or a non-bonded molecule X (i.e. A_0 or B), with $\frac{1}{2} q(q-1)$ and q different bond orientations for A_2 and A_1, respectively. Arbitrary distributions of A_2 and A_1 molecules on the lattice are not all acceptable, however. Consider the lattice graph G formed by the V sites and the $\frac{1}{2} q V$ edges joining first neighbouring sites; configurations counted in $h(N_1, N_2)$ are such that all edges of G are occupied either in a directly compatible way (DC) or in an indirectly compatible way (IC), as defined in table 1. We may then write

$$h(N_1, N_2) = \sum_{C(N_1, N_2)} \prod_{ij} A(s_i, s_j) \tag{2.3}$$

where we sum over all configurations C, acceptable or not, and the product includes all edges of G, with

$$A(s_i, s_j) = 1 \qquad \text{if } (s_i, s_j) \in \text{DC or IC}$$

$$= 0 \qquad \text{if } (s_i, s_j) \in \text{I (incompatible).}$$

See table 1. As each acceptable configuration exactly contains $\frac{1}{2} N_1 + N_2$ edges DC and $\frac{1}{2} q V - \frac{1}{2} N_1 - N_2$ edges IC, (2.3) may be rewritten as

$$h(N_1, N_2) = (1 + a_{IC})^{-qV/2} [(1 + a_{IC})/(1 + a_{DC})]^{N_1/2 + N_2} \sum_{C(N_1, N_2)} \prod_{ij} [1 + a(s_i, s_j)] \tag{2.4}$$

Table 1. Site and edge occupancies.

	Site i			Edge ij	
s_i	Representation	Bond orientations	s_i, s_j	Compatibility	
A_2		$q(q-1)/2$		Directly compatible (DC)	
A_1		q			
$X = A_0$ or B		none		Indirectly compatible (IC)	

On the right-hand side of this table, a cross means that site i (or j) is occupied by X, A_1 or A_2, with no bond issued from i to j (or j to i) i.e.

Incompatible (I)

where

$$a(s_i, s_j) = a_{DC} \qquad \text{for } (s_i, s_j) \in DC$$
$$= a_{IC} \qquad \text{for } (s_i, s_j) \in IC \qquad (2.5)$$
$$= -1 \qquad \text{for } (s_i, s_j) \in I.$$

Expression (2.4) provides the starting point of a weak subgraph expansion (the values of a_{DC} and a_{IC} will be conveniently fixed in the next section). Substituting (2.4) into (2.1) gives

$$\Omega = [(z_A + z_B)(1 + a_{IC})^{-q/2}]^V \sum_{N_1} \sum_{N_2} a_1^{N_1} a_2^{N_2} \sum_{C(N_1, N_2)} \prod_{ij} [1 + a(s_i, s_j)] \qquad (2.6)$$

with

$$a_1 = zy_1[(1 + a_{IC})/(1 + a_{DC})]^{1/2}$$
$$a_2 = zy_2(1 + a_{IC})/(1 + a_{DC}). \qquad (2.7)$$

We next associate a normalised weight $b(s)$ to the occupation of each site:

$$b(A_2) = a_2[1 + qa_1 + \tfrac{1}{2}q(q-1)a_2]^{-1},$$
$$b(A_1) = a_1[1 + qa_1 + \tfrac{1}{2}q(q-1)a_2]^{-1},$$
$$b(X) = [1 + qa_1 + \tfrac{1}{2}q(q-1)a_2]^{-1}$$

(see table 1). This leads to

$$\Omega = \{(z_A + z_B)[1 + qa_1 + \tfrac{1}{2}q(q-1)a_2](1 + a_{IC})^{-q/2}\}^V \sum_C \prod_i b(s_i) \prod_{ij} [1 + a(s_i, s_j)], \qquad (2.8)$$

where the sum includes all configurations C, acceptable or not, with any number of A_1 and A_2 molecules. Expanding the last product of this sum, we obtain the series

$$\sum_C \prod_i b(s_i)\left(1 + \sum_{ij} a(s_i, s_j) + \sum_{ij}\sum_{kl} a(s_i, s_j)a(s_k, s_l) + \dots\right),$$

each term of which matches that particular subgraph g of G which includes the corresponding edges and their adjacent sites (g may involve disconnected parts but no isolated sites). Hence, taking advantage of the normalisation of $b(s)$, the last expression may be rewritten as a sum of weighted subgraphs of G

$$1 + \sum_{g \subseteq G} W(g) \tag{2.9}$$

with

$$W(g) = \sum_{s_i} \ldots \sum_{s_l} b(s_i) \ldots b(s_l) a(s_i, s_j) \ldots a(s_k, s_l)$$

for g including edges $(ij) \ldots (kl)$. As $W(g)$ merely depends on the topology of g, expression (2.9) may be transformed into

$$1 + \sum (g; G) W(g)$$

where g is now any graph (devoid of isolated sites) and $(g; G)$ is the number of subgraphs of G isomorphic to g, i.e. the number of weak embeddings of g in G (Essam and Fisher 1970). Generally speaking, $(g; G)$ is a polynomial in V, the degree of which equals the number of disconnected pieces of g and, due to a general theorem for homogeneous lattices (Domb 1960 pp 220–5), one has

$$1 + \sum_g (g; G) W(g) = \exp\left(V \sum_g (g; G)_1 W(g) \right)$$

where $(g; G)_1$ is the coefficient of the term of degree one in V. Combining with (2.8), we finally obtain

$$\Omega^{1/V} = (z_A + z_B)[1 + qa_1 + \tfrac{1}{2}q(q-1)a_2](1 + a_{1C})^{-q/2} \exp(F) \tag{2.10}$$

where

$$F = \sum_g (g; G)_1 W(g). \tag{2.11}$$
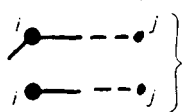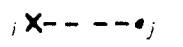
3. Weighting the graphs

Consider the factorisation

$$a(s_i, s_j) = c_{ij}(s_i) c_{ji}(s_j) \tag{3.1}$$

where $c_{ij}(s_i)$ can take two values, c_0 and c_1, corresponding to the situations described in table 2. It follows, from (2.5)

$$a_{DC} = c_1^2 \qquad a_{1C} = c_0^2 \qquad -1 = c_0 c_1 \tag{3.2}$$

Table 2. Values of $c_{ij}(s_i)$ for various states of site i, independently of the state of site j.

s_i	$c_{ij}(s_i)$
$\left.\begin{array}{c} i\!\bullet\!\!-\!\!-\!\!-\!\!\bullet\, j \\ i\,\bullet\!\!-\!\!-\!\!-\!\!\bullet\, j \end{array}\right\}$	c_1
$i\,\mathbf{X}\!-\!-\!-\!-\!\bullet\, j$	c_0

and next, from (2.7)

$$a_1 = zy_1 c_0 \qquad a_2 = zy_2 c_0^2. \tag{3.3}$$

On account of the factorised form (3.1), $W(g)$ may now be expressed as a product of weights associated to each site of g, i.e.

$$W(g) = \prod_{i \subset g} \left[\sum_{s_i} \left(b(s_i) \prod_j c_{ij}(s_i) \right) \right],$$

where the last product involves all edges of g incident with site i. This can be rewritten as

$$W(g) = \prod_{d=1}^{q} w(d)^{v_d(g)} \tag{3.4}$$

where $v_d(g)$ is the number of sites of degree d in g (the degree of a site is the number of edges incident with it) and $w(d)$ is the corresponding weight of such a site (labelled as 1):

$$w(d) = \sum_{s_1} \left(b(s_1) \prod_j c_{1j}(s_1) \right).$$

The evaluation of $w(d)$ is straightforward:

$$w(d) = c_0^{d-2}[1 + qa_1 + \tfrac{1}{2}q(q-1)a_2]^{-1}\{c_0^2 + a_1 c_0[dc_1 + (q-d)c_0] $$
$$ + a_2[\tfrac{1}{2}d(d-1)c_0^2 + d(q-d)c_0 c_1 + \tfrac{1}{2}(q-d)(q-d-1)c_1^2]\}$$

or, on account of $c_1 = -1/c_0$,

$$w(d) = c_0^d\{1 - [1 + qa_1 + \tfrac{1}{2}q(q-1)a_2]^{-1}d(1+c_0^{-2})[a_1 + (q-1)a_2 - \tfrac{1}{2}(d-1)(1+c_0^{-2})a_2]\}. \tag{3.5}$$

The parameter c_0, which is still arbitrary, will now be fixed by imposing $w(1) = 0$; this condition nullifies the weights of all graphs with sites of degree one and considerably simplifies the evaluation of F. It then follows, from (3.5)

$$(1 + c_0^{-2})[a_1 + (q-1)a_2] = 1 + qa_1 + \tfrac{1}{2}q(q-1)a_2, \tag{3.6}$$

so that

$$w(d) = (d-1)c_0^d\{\tfrac{1}{2}d(1+c_0^{-2})a_2[a_1 + (q-1)a_2]^{-1} - 1\}.$$

The combination of (3.6) with (3.3) leads to the following relationship between c_0 and z:

$$z = c_0\{y_1[1 - (q-1)c_0^2] + y_2 c_0(q-1)[1 - \tfrac{1}{2}(q-2)c_0^2]\}^{-1}.$$

In the limit of low z (low concentration of A), one has $c_0 \approx zy_1$; we shall therefore eliminate c_0 everywhere in terms of the more convenient variable $x = c_0/y_1$. This gives

$$z = x\{1 - x^2 y_1^2(q-1) + xy_2(q-1)[1 - \tfrac{1}{2}(q-2)x^2 y_1^2]\}^{-1} \tag{3.7}$$

and

$$w(d) = (d-1)x^{d-1}y_1^{d-2}\{\tfrac{1}{2}dy_2(1+x^2 y_1^2)[1 + xy_2(q-1)]^{-1} - xy_1^2\}. \tag{3.8}$$

Not only does x tend to z at sufficiently low values but it becomes strictly identical to z when both y_1 and y_2 equal zero (ideal mixture of A and B).

As a final step, we rewrite the grand partition function (2.10) in terms of x, with the result

$$\ln \Omega^{1/V} = [\ln(z_A + z_B) + L(x; y_1, y_2)] + F(x; y_1, y_2) \tag{3.9}$$

with

$$\exp L(x; y_1, y_2) = (z/x)[1 + xy_2(q-1)](1 + x^2 y_1^2)^{1-(q/2)}. \tag{3.10}$$

This completes the formalism: $\ln \Omega^{1/V}$ appears as the sum of two terms, the first one expressed in close form and the second one expandable according to graphological prescriptions.

4. Thermodynamic properties

The molar fractions x_A, x_B follow from the general formula

$$x_B = 1 - x_A = z_B(\partial/\partial z_B) \ln \Omega^{1/V},$$

which, when applied to (3.9), gives, on account of (2.2)

$$x_B = (1 - z)[1 - (d/d \ln z)(L + F)]. \tag{4.1}$$

The chemical potentials μ_A, μ_B are related to z_A, z_B by the expression

$$\mu_A - \mu_B = kT \ln(z_A/z_B) \tag{4.2}$$

and they must also satisfy the Gibbs–Duhem equation

$$x_A \, d\mu_A + x_B \, d\mu_B = 0.$$

It then follows that

$$d\mu_A = x_B d(\mu_A - \mu_B) = kTx_B \, d \ln(z_A/z_B)$$

$$= kTx_B \, d \ln[z/(1-z)] = kTx_B(1-z)^{-1} \, d \ln z.$$

Combining with (4.1), we obtain

$$d\mu_A = kT \, d(\ln z - L - F)$$

and finally, by putting the integration constant to zero,

$$\mu_A/kT = \ln z - L - F. \tag{4.3}$$

This implies also, on account of (4.2)

$$\mu_B/kT = \ln(1-z) - L - F. \tag{4.4}$$

Consider the limiting situation of an ideal mixture, i.e. $y_1 = y_2 = 0$, in which case $z = x$ while L and F trivially vanish; it follows from (4.1) that $x_A = 1 - x_B = z$, so that (4.3) and (4.4) reduce to

$$\mu_A^{id}/kT = \ln x_A \qquad \mu_B^{id}/kT = \ln x_B.$$

In order to measure the non-ideality of the mixture, we shall introduce the so-called excess chemical potentials μ_A^e and μ_B^e, defined as $\mu_A - \mu_A^{id}$ and $\mu_B - \mu_B^{id}$; this gives, in the present case

$$\mu_A^e/kT = \ln(z/x_A) - L - F, \tag{4.5}$$

$$\mu_B^e/kT = \ln[(1-z)/x_B] - L - F. \tag{4.6}$$

Table 3. Weak subgraphs of the simple cubic lattice, up to $n = 8$, with all sites of degree 2 at least.
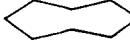
n	Subgraph	$(g; G)_1$
4		3
6		22
7		18
8		207
		24
		30
		$-\frac{99}{2}$

Table 4. Excess chemical potential μ_A^e computed at various levels of approximation (simple cubic lattice).

(a) $y_1 = 10$, $y_2 = 10$

			μ_A^e/kT		
x_A	Zeroth	$n = 4$	$n = 6$	$n = 8$	$n = 10$
0.2	−2.440 03	−2.438 24	−2.437 97	−2.437 93	−2.437 91
0.4	−2.923 80	−2.923 29	−2.923 26	−2.923 22	−2.923 20
0.6	−3.147 74	−3.147 74	−3.147 74	−3.147 74	−3.147 74
0.8	−3.252 73	−3.253 29	−3.253 33	−3.253 34	−3.253 34
1.0	−3.282 96	−3.285 60	−3.286 18	−3.286 43	−3.286 53

(b) $y_1 = 1$, $y_2 = 10$

			μ_A^e/kT		
x_A	Zeroth	$n = 4$	$n = 6$	$n = 8$	$n = 10$
0.2	−2.264 60	−2.259 69	−2.258 68	−2.258 28	−2.257 95
0.4	−2.788 85	−2.787 88	−2.787 81	−2.787 67	−2.787 61
0.6	−3.027 21	−3.027 21	−3.027 21	−3.027 21	−3.027 21
0.8	−3.138 06	−3.138 77	−3.138 82	−3.138 84	−3.138 84
1.0	−3.169 85	−3.173 33	−3.174 20	−3.174 64	−3.174 84

(Note that both μ_A^e and μ_B^e tend to zero at vanishing concentration of A.) Owing to the complexity of the expressions of z, L and F in terms of x, the values of μ_A^e and μ_B^e, as functions of x_A, cannot be obtained analytically. The standard procedure, for a specified value of x_A, is to solve (4.1) numerically for x and then to calculate the corresponding values of μ_A^e and μ_B^e.

5. Numerical analysis of the model

Our aim now will be to see to what extent the formalism developed so far is useful in practice for computing the thermodynamic properties of the model. Obviously, the evaluation of F is a tedious task which cannot possibly be carried out beyond a certain level of complexity of the lattice subgraphs. What we may hope is that, for at least some range of the parameters y_1, y_2, the contribution of F to the thermodynamic properties converges rapidly when the subgraphs get larger (or is even negligible). This expectation is not unrealistic: such a situation is precisely met for the ice model and the monomer-dimer model, when treated by the kind of formalism we use here (Nagle 1966a, b, Gaunt 1969).

Our strategy will be as follows: for a given lattice, we group together the contributions of all subgraphs with the same number of edges n; we then compute F to various levels of approximation F_n, by including the contributions of all graphs with n edges or less, and we proceed further to obtain the excess chemical potentials to the same order in n. Because all sites of the relevant subgraphs must be of degree two at least, the first one to appear is the shortest cycle realisable on the lattice (which means $n = 4$ for the simple cubic lattice). As zeroth approximation we simply put F equal to zero or, equivalently, we treat the lattice as if it contained no cycle path at all. The topological meaning of this approximation is that we replace the actual lattice by a Bethe (pseudo-) lattice with the same coordination number q.

As an illustration, consider the simple cubic lattice; the relevant graphs are listed in table 3 (with their embedding numbers) up to $n = 8$. The excess chemical potential μ_A^e, obtained numerically, is quoted in table 4, for different levels of approximation n. For the two cases considered, $y_1 = y_2 = 10$ and $y_1 = 1$, $y_2 = 10$, it is quite clear that, when going from the zeroth approximation to higher ones, there is hardly a change in μ_A^e. More extensive numerical work, on the simple cubic lattice and other ones as well, has shown that for most values of y_1, y_2, which are physically compatible with the strength of hydrogen bonds, the zeroth approximation is very satisfactory.

There exists however one pathological situation where it leads to a complete failure: when y_1 equals exactly zero, molecules will only polymerise in cycles and, as no cycles are possible on a Bethe lattice, L vanishes exactly and it is precisely F which is the relevant term in this case.

6. Final remarks

The fact that the zeroth approximation works well for this model is encouraging; in a forthcoming paper, we will compare the model to some real systems and also to some of the so-called 'chemical' theories. We also intend to generalise the formalism in order to treat more complicated bonding effects (e.g. B being able to associate with A) and to include surface terms.

Acknowledgments

References

Abraham D B and Heilman O J 1972 *J. Stat. Phys.* **4** 15
—— 1975 *J. Stat. Phys.* **13** 461
Domb C 1960 *Adv. Phys.* **9** 150
Essam J W and Fisher M E 1970 *Rev. Mod. Phys.* **42** 271
Gaunt D S 1969 *Phys. Rev.* **179** 174
Nagle J F 1966a *J. Math. Phys.* **7** 1484
—— 1966b *Phys. Rev.* **152** 190
Prigogine I, Defay R and Everett D H 1956 *Chemical Thermodynamics* (London: Longmans Green)