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Surface tension of binary mixtures: an exact relation within SOS-like models

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Abstract

We investigate the statistical mechanics of binary mixtures within the framework of a two-component SOS-model, where we obtain an exact formula for the free energy. This allows for an explicit expression linking the surface tension of a binary mixture to those of its components which is valid at all temperatures, answering an open question asked by De Coninck *et al* (2005 *J. Stat. Phys.* **119** 597–642).

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1. Introduction

The notion of surface tension or free energy per unit area plays a key role in many applications involving surface phenomena and phase coexistence. When one considers a fluid which is a mixture of two chemical species 1 and 2 in equilibrium with its vapour, one of the first theoretical and experimental problems is to determine how the surface tension τ_{12} of the mixture depends on its composition. In the literature, several equations corresponding to different assumptions have been obtained from thermodynamic considerations. As one would expect, they give the surface tension τ_{12} as a function of the surface tensions τ_1 and τ_2 of species 1 and 2 when they are chemically pure.

Thus, for ideal or nearly ideal solutions, a fairly simple thermodynamical treatment due to Guggenheim [17] leads to the following equation,

$$e^{-\beta a \tau_{12}} = c_1 e^{-\beta a \tau_1} + c_2 e^{-\beta a \tau_2}, \quad (1.1)$$

where c_1 is the fixed molar fraction of species 1 in the mixture, $c_2 = 1 - c_1$ the molar fraction of species 2, a is the mean distance between molecules, and $\beta = \frac{1}{kT}$ is the inverse temperature.

Another treatment by Eberhart [14] assumes that the surface tension of a binary solution is linear in the surface composition, that is

$$\tau_{12} = c_1^s \tau_1 + c_2^s \tau_2 \quad (1.2)$$

where c_i^s , $i = 1, 2$, denote the molar fraction of species i near the surface of phase separation.

It is moreover assumed that the ratio $\frac{c_1^s}{c_1}$ is proportional to the ratio $\frac{c_2^s}{c_2}$.

Still other equations have been proposed by Szykowski [26] as well as Defay and Prigogine [10]. For a detailed review on the subject we refer the reader to Adamson's book [1] (chapter III, section 4) and references therein. See also the monograph by Defay, Prigogine and coworkers [11].

From a microscopic point of view, the problem was investigated by De Coninck and Ruiz [9], who devised a two-valued random interaction to describe the phase boundary. The surface tension for that model could then be computed and according to whether one considers an annealed or quenched disorder, one recovers equations (1.1) and (1.2) respectively.

More recently, De Coninck *et al* [8] introduced a lattice-gas model for which they were able to obtain a low-temperature relationship linking the surface tension of the mixture with those of the pure species. They considered a two- or three-dimensional system with two kinds of particles, where each lattice site can be in one of the three states 0, 1, 2, interpreted respectively as an empty site, a site occupied by a particle of the first kind, and a site occupied by a particle of the second kind. If one allows only for particles 1 (resp. 2) in the model, the system reduces to the usual Ising model with coupling constant $\frac{J_1}{2}$ (resp. $\frac{J_2}{2}$), where the surface tensions τ_1 (resp. τ_2) for the pure species are obtained. The surface tension τ_{12} of the mixture is defined in the unrestricted three-state model. The latter can be studied in the phase coexistence region with the help of Pirogov–Sinai theory, leading to the following equation which is valid at low temperatures:

$$e^{-\beta(\tau_{12}-\mathcal{F})} = c_1^* e^{-\beta(\tau_1-\mathcal{F}_1)} + c_2^* e^{-\beta(\tau_2-\mathcal{F}_2)}. \quad (1.3)$$

Here \mathcal{F}_i , ($i = 1, 2$) is the specific energy of the gas of ‘jumps’ describing the Gallavotti line of phase separation for the two-dimensional Ising model [15], and that of the gas of ‘walls’ describing the Dobrushin interface in three dimensions [13]. This means that $\tau_1 - \mathcal{F}_1 = J_1$ and $\tau_2 - \mathcal{F}_2 = J_2$ are the respective energy costs per unit length or unit area of the 1|0 and 2|0 interfaces. The quantity \mathcal{F} is the specific energy of a gas of geometrical objects called aggregates, which can be expressed as a convergent series at low temperatures. Finally, c_1^* and c_2^* are some constants which can be explicitly computed in terms of the concentrations c_1 and c_2 , the coupling constants J_1 and J_2 , the inverse temperature β as well as the dimension d .

De Coninck *et al* pointed out that it would be an interesting problem to obtain an exact expression for the surface tension τ_{12} of the mixture in the solid-on-solid (SOS) approximation of the two-dimensional model. This allows indeed for a formula which is not restricted to low temperatures, linking the surface tension of the mixture to those of the pure species, their respective concentrations c_1 and c_2 , as well as the inverse temperature.

The aim of the present paper is to address this problem. By taking the anisotropic limit where one lets the vertical coupling constants tend to infinity with an appropriate normalization, we obtain indeed a two-component (SOS) approximation of the model which captures the essential features of the interface. The surface tension τ_{12} of the mixture is the free energy density of this model. Similarly, the surface tensions τ_1 and τ_2 of the pure species are obtained from the latter SOS model if one allows only particles of species 1 (resp. 2). As a main result, we solve the question pointed out above by obtaining an exact formula for the free energy per unit length of the two-component SOS model.

The paper is organized as follows: in section 2, we introduce the model and state our main result. Section 3 is devoted to the proof. Concluding remarks are given in section 4.

2. Definitions and main result

We consider a two-dimensional square lattice \mathbb{Z}^2 , to each site $x \in \mathbb{Z}^2$ of which we associate a variable σ_x taking values in the set $\Omega = \{0, 1, 2\}$. We say that a site is empty if $\sigma_x = 0$ and that it is occupied by a particle of type 1 or of type 2 if $\sigma_x = 1$ or 2. The Hamiltonian of the system is given by

$$H = \sum_{\langle x,y \rangle} [(J_1 + J_{xy})(\delta(\sigma_x, 1)\delta(\sigma_y, 0) + \delta(\sigma_x, 0)\delta(\sigma_y, 1)) + (J_2 + J_{xy})(\delta(\sigma_x, 2)\delta(\sigma_y, 0) + \delta(\sigma_x, 0)\delta(\sigma_y, 2))] \tag{2.1}$$

where the sum runs over nearest-neighbour pairs $\langle x, y \rangle$, and δ is the usual Kronecker symbol: $\delta(\sigma, \sigma') = 1$ if $\sigma = \sigma'$ and $\delta(\sigma, \sigma') = 0$ otherwise. J_1 and J_2 are positive coupling constants. Finally, J_{xy} is an anisotropic coupling constant which takes the value $J \geq 0$ if $\langle x, y \rangle$ is a vertical nearest-neighbour pair (i.e. if $x = y \pm (0, 1)$) and 0 otherwise.

In the box $\Lambda \subset \mathbb{Z}^2$, the grand canonical partition function with boundary conditions (b.c.) is defined by

$$Z_{\Lambda}^{b.c.} = \sum_{\sigma_{\Lambda} \in \Omega^{\Lambda}} \exp \left(-\beta H_{\Lambda}(\sigma_{\Lambda}) + \mu_1 \sum_{x \in \Lambda} \delta(\sigma_x, 1) + \mu_2 \sum_{x \in \Lambda} \delta(\sigma_x, 2) \right) \chi^{b.c.}(\sigma_{\Lambda}) \tag{2.2}$$

where $\beta = 1/kT$ stands for the inverse temperature, $\mu_1, \mu_2 \in \mathbb{R}$ are chemical potentials, $H_{\Lambda}(\sigma_{\Lambda})$ is the Hamiltonian (2.1) with the sum running over nearest-neighbour pairs $\langle x, y \rangle \subset \Lambda$, and $\chi^{b.c.}(\sigma_{\Lambda})$ is a characteristic function standing for the boundary condition b.c. We shall be interested in particular in the following boundary conditions within the box $\Lambda \equiv \{(x_1, x_2) \in \mathbb{Z}^2 : |x_1| \leq N, |x_2| \leq M\}$:

- the empty boundary condition: $\chi_{\Lambda}^0(\sigma_{\Lambda}) = \prod_{x \in \partial \Lambda} \delta(\sigma_x, 0)$;
- the mixed boundary condition: $\chi_{\Lambda}^{mix}(\sigma_{\Lambda}) = \prod_{x \in \partial \Lambda} (1 - \delta(\sigma_x, 0))$;
- the free boundary condition: $\chi_{\Lambda}^{fr}(\sigma_{\Lambda}) = 1$;
- the mixed-empty boundary condition: $\chi_{\Lambda}^{mix,0}(\sigma_{\Lambda}) = \prod_{x \in \partial_u \Lambda} \delta(\sigma_x, 0) \prod_{x \in \partial_l \Lambda} (1 - \delta(\sigma_x, 0))$.

Here the boundary $\partial \Lambda$ of Λ is the set of sites in Λ which have a nearest neighbour in $\Lambda^c = \mathbb{Z}^2 \setminus \Lambda$, and we use $\partial_u \Lambda \equiv \{(x_1, x_2) \in \partial \Lambda : x_2 > 0\}$ to denote the upper boundary of Λ , and $\partial_l \Lambda \equiv \partial \Lambda \setminus \partial_u \Lambda$ to denote the lower boundary of Λ .

We next introduce the associated finite volume Gibbs measures (specifications) defined by

$$\mathbb{P}_{\Lambda}^{b.c.}(\sigma_{\Lambda}) = \frac{e^{-\beta \tilde{H}_{\Lambda}(\sigma_{\Lambda})} \chi^{b.c.}(\sigma_{\Lambda})}{Z_{\Lambda}^{b.c.}} \tag{2.3}$$

where

$$\tilde{H}_{\Lambda}(\sigma_{\Lambda}) = H_{\Lambda}(\sigma_{\Lambda}) - \frac{\mu_1}{\beta} \sum_{x \in \Lambda} \delta(\sigma_x, 1) - \frac{\mu_2}{\beta} \sum_{x \in \Lambda} \delta(\sigma_x, 2). \tag{2.4}$$

They determine by the Dobrushin–Lanford–Ruelle equations the set of Gibbs states $\mathcal{G}_{\beta}(\tilde{H})$ on \mathbb{Z}^2 corresponding to the Hamiltonian \tilde{H} at inverse temperature β (see, e.g., [23, 25]). Whenever the weak limit $\lim_{\Lambda \uparrow \mathbb{Z}^2} \mathbb{P}_{\Lambda}^{b.c.}$ exists, it belongs to $\mathcal{G}_{\beta}(\tilde{H})$ and we shall call it the Gibbs state with boundary condition b.c.

In the limit $J \rightarrow +\infty$, The Gibbs state with empty boundary conditions is concentrated on the configuration with empty sites:

$$\lim_{J \rightarrow \infty} \mathbb{P}_{\Lambda}^0(\sigma_{\Lambda}) = \prod_{x \in \Lambda} \delta(\sigma_x, 0). \tag{2.5}$$

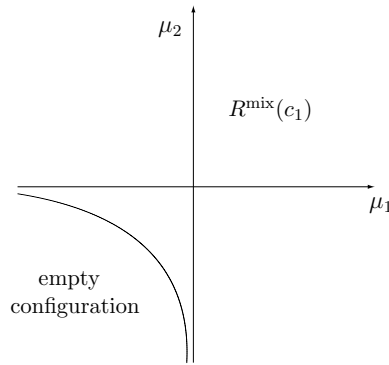


Figure 1. Coexistence line of the mixture with its vapour.

Let moreover

$$R_{\Lambda}^{\text{mix}} = \{\sigma_{\Lambda} \in \Omega^{\Lambda} : \forall x \in \Lambda, \sigma_x \neq 0\} \tag{2.6}$$

be the restricted ensemble of configurations in Λ with no empty sites. In the limit $J \rightarrow +\infty$, the finite volume Gibbs measure with mixed boundary conditions is immediately seen to be concentrated on R_{Λ}^{mix} :

$$\lim_{J \rightarrow +\infty} \mathbb{P}_{\Lambda}^{\text{mix}}(\sigma_{\Lambda}) = \begin{cases} \frac{e^{\mu_1 N_1} e^{\mu_2 (|\Lambda| - N_1)}}{(e^{\mu_1} + e^{\mu_2})^{|\Lambda|}} & \text{if } \sigma_{\Lambda} \in R_{\Lambda}^{\text{mix}} \\ 0 & \text{otherwise} \end{cases} \tag{2.7}$$

where N_1 denotes the number of sites x in Λ for which $\sigma_x = 1$. Furthermore, if $R_{\Lambda}^{\text{mix}}(c_1)$, $0 \leq c_1 \leq 1$, is the subset of configurations in R_{Λ}^{mix} with exactly $[c_1|\Lambda|] = N_1$ sites occupied by a particle of species 1 ($[\cdot]$ stands for the entire part), (2.7) directly implies that the latter finite volume Gibbs measure is uniform on each $R_{\Lambda}^{\text{mix}}(c_1)$ and that

$$\lim_{J \rightarrow +\infty} \mathbb{P}_{\Lambda}^{\text{mix}}(R_{\Lambda}^{\text{mix}}(c_1)) = \frac{\binom{|\Lambda|}{N_1} e^{\mu_1 N_1} e^{\mu_2 (|\Lambda| - N_1)}}{(e^{\mu_1} + e^{\mu_2})^{|\Lambda|}} \tag{2.8}$$

where $\binom{|\Lambda|}{N_1}$ denotes a binomial coefficient. Elementary considerations (see, e.g., [8]) then show that in the thermodynamic limit the right-hand side of (2.8) tends to one iff

$$c_1 = \frac{e^{\mu_1}}{e^{\mu_1} + e^{\mu_2}}. \tag{2.9}$$

The Gibbs state with mixed boundary conditions is thus concentrated on the set $R^{\text{mix}}(c_1)$ of configurations in $\Omega^{\mathbb{Z}^2}$ with concentration c_1 of particles of species 1 given by (2.9).

For the free boundary condition one shows that

$$\lim_{J \rightarrow +\infty} \mathbb{P}_{\Lambda}^{\text{fr}}(\sigma_{\Lambda}) = \frac{1}{1 + (e^{\mu_1} + e^{\mu_2})^{|\Lambda|}} \lim_{J \rightarrow +\infty} \mathbb{P}_{\Lambda}^0(\sigma_{\Lambda}) + \frac{1}{1 + (e^{\mu_1} + e^{\mu_2})^{-|\Lambda|}} \lim_{J \rightarrow +\infty} \mathbb{P}_{\Lambda}^{\text{mix}}(\sigma_{\Lambda}). \tag{2.10}$$

Hence, one deduces from the above considerations that the configuration with empty sites coexists with the restricted ensemble $R^{\text{mix}}(c_1)$ as soon as $e^{\mu_1} + e^{\mu_2} = 1$. The corresponding phase diagram is shown in figure 1.

From now on we place ourselves in the phase coexistence region by setting $e^{\mu_1} + e^{\mu_2} = 1$ and introduce the surface tension between the mixture and its vapour:

$$\tau_{12} \equiv - \lim_{N \rightarrow +\infty} \frac{1}{\beta(2N+1)} \lim_{M \rightarrow +\infty} \lim_{J \rightarrow +\infty} \ln \left(\frac{e^{\beta J(2N+1)} Z_{\Lambda}^{\text{mix},0}}{(Z_{\Lambda}^0 Z_{\Lambda}^{\text{mix}})^{\frac{1}{2}}} \right). \tag{2.11}$$

The latter equation also defines the surface tension τ_1 of the pure species 1 by setting $c_2 = 0$ (i.e. by taking the limit $\mu_2 \rightarrow -\infty$) for all the partition functions. The surface tension τ_2 of the species 2 is defined similarly. We are now ready to state the main result of this paper:

Theorem 1. *Let $\mu_1, \mu_2 \in \mathbb{R}$ be chemical potentials satisfying*

$$e^{\mu_1} + e^{\mu_2} = 1 \tag{2.12}$$

and let moreover

$$F_k = e^{\mu_1} e^{-k\beta J_1} + e^{\mu_2} e^{-k\beta J_2}, \quad k \in \{1, 2, 3\} \tag{2.13}$$

where $\beta > 0$ is the inverse temperature and J_1, J_2 are positive coupling constants. Then, the surface tension defined by (2.11) reads

$$\tau_{12} = -\frac{1}{\beta} \left\{ \ln \left(\frac{F_2}{2(1-F_1)} \right) + \ln \left(2 + \frac{1-F_1}{F_2 F_1^{-1}} + \sqrt{\left(2 + \frac{1-F_1}{F_2 F_1^{-1}} \right)^2 + 4 \left(\frac{F_3 F_2^{-2} F_1 (1-F_1^2)}{1-F_2} - 1 \right)} \right) \right\}. \tag{2.14}$$

3. Proof

3.1. Interfaces

We first of all note that

$$\lim_{J \rightarrow +\infty} Z_{\Lambda}^0 = \lim_{J \rightarrow +\infty} Z_{\Lambda}^{\text{mix}} = 1. \tag{3.1}$$

Let moreover $\Omega_{\text{mix},0}^{\Lambda}$ be the set of configurations in Λ belonging to the support of $\chi^{\text{mix},0}(\cdot)$. It is easily seen that in the limit $J \rightarrow +\infty$, only those configurations contribute to the partition function $\lim_{J \rightarrow +\infty} e^{\beta J(2N+1)} Z_{\Lambda}^{\text{mix},0}$ that lie in the set

$$\Omega_{\text{SOS}}^{\Lambda} \equiv \left(\sigma \in \Omega_{\text{mix},0}^{\Lambda} : \forall i \in \{-N, \dots, N\} \exists h_i \in \{-M, \dots, M\} : \begin{cases} \sigma_{(i,h)} = 0 & \text{if } h > h_i \\ \sigma_{(i,h)} \neq 0 & \text{if } h \leq h_i \end{cases} \right) \tag{3.2}$$

i.e. the set of configurations which on each vertical line are non-empty up to a certain height and empty above. Note that for every $\sigma \in \Omega_{\text{mix},0}^{\Lambda}$ one has automatically $h_{-N} = h_N = 0$.

We introduce the *dual bond* of a given unit-bond $\langle x, y \rangle$ as the unique unit-bond $\langle x, y \rangle^*$ in \mathbb{R}^2 which intersects $\langle x, y \rangle$ in the middle and is orthogonal to it. The dual of a set of bonds B , i.e. the collection of dual bonds corresponding to some bond in B , will be denoted by B^* hereafter.

Now let $\mathcal{H} \equiv \{h_i \in \mathbb{Z}\}_{i \in \{-N, \dots, N\}}$ be a given collection of heights such that $h_{-N} = h_N = 0$, and let $\Omega_{\mathcal{H}}$ be the set of configurations on $\{-N, \dots, N\} \times \mathbb{Z}$ satisfying the condition displayed

in (3.2) for this set of heights. Let moreover σ be some configuration in $\Omega_{\mathcal{H}}$ and $L(I)$ be the set of bonds $\langle x, y \rangle$ in \mathbb{Z}^2 for which $\sigma_x \neq 0$ and $\sigma_y = 0$. This notion does not depend on the particular choice for σ . We will hereafter call *SOS-interface I of width N associated with \mathcal{H}* the dual $I \equiv L^*(I)$ of $L(I)$. Conversely, any set of bonds $I \subset \mathbb{R}^2$ which is the interface associated with some collection of heights \mathcal{H} will be called an interface. In this case $L(I) \equiv I^*$. The *set of sites of the interface I* is moreover defined as the set $S(I)$ of sites $x \in \mathbb{Z}^2$ which belong to some bond in $L(I)$ and which satisfy $\sigma_x \neq 0$. Again, this notion does not depend on the particular choice for σ .

The notion of interface is thus purely geometrical: it is a connected line starting at the origin and returning to the origin without overhangs. Specifying an interface I is equivalent to specifying a set of heights \mathcal{H} . We will hereafter denote the set of interfaces of width N by \mathcal{I}_N . For a given interface I we also introduce the shorthand notation:

$$\Omega_I \equiv \{\sigma \in \Omega^{S(I)} : \forall x \in S(I), \sigma_x \neq 0\}. \tag{3.3}$$

If $\sigma \in \Omega_I$ for some interface I , let $S_1(I)$ be the set of sites x belonging to $S(I)$ such that $\sigma_x = 1$ and let $L_1(I)$ be the set of bonds in $L(I)$ which have an end-point in $S_1(I)$. Let moreover $S_2(I) = S(I) \setminus S_1(I)$ and $L_2(I) = L(I) \setminus L_1(I)$. It is now easily seen that the identity

$$Z_{\text{SOS}}^N \equiv \lim_{M \rightarrow +\infty} \lim_{J \rightarrow +\infty} e^{\beta J(2N+1)} Z_{\Lambda}^{\text{mix},0} = \sum_{I \in \mathcal{I}_N} \sum_{\sigma_I \in \Omega_I} \omega_I(\sigma_I) \tag{3.4}$$

where

$$\omega_I(\sigma_I) \equiv e^{\mu_1 |S_1(I)|} e^{\mu_2 |S_2(I)|} e^{-\beta J_1 |L_1(I)|} e^{-\beta J_2 |L_2(I)|} \tag{3.5}$$

holds. Hereafter we use the notation $|E|$ to denote the cardinality of the set E .

Equation (3.4) can be written in a slightly more compact form: let the *envelope $E(S)$* of a set of sites $S \subset \mathbb{Z}^2$ be the set of bonds in \mathbb{Z}^2 which have at least one endpoint in S . The weight-factor (3.5) can equivalently be written as

$$\omega_I(\sigma_I) = \prod_{x \in S(I)} f(x, \sigma_x) \tag{3.6}$$

where

$$f(x, \sigma_x) \equiv e^{\mu_{\sigma_x}} e^{-\beta J_{\sigma_x} |E^*(x) \cap I|}. \tag{3.7}$$

Summing over all the possible configurations, we obtain the contracted weight,

$$\omega_c(I) \equiv \sum_{\sigma_I \in \Omega_I} \omega_I(\sigma_I) = \prod_{x \in S(I)} f(x) \tag{3.8}$$

with

$$f(x) \equiv \sum_{\sigma_x \in \{1,2\}} f(x, \sigma_x) \tag{3.9}$$

Note that since $\beta J_{\sigma_x} > 0$; $\sigma_x \in \{1, 2\}$, and $e^{\mu_1} + e^{\mu_2} = 1$, we have $f(x) < 1$ for any site $x \in S(I)$. Let us moreover call a site $x \in S(I)$ of *type k* iff

$$|E^*(x) \cap I| = k.$$

Since I is a two dimensional SOS-interface, k can only take the values $\{1, 2, 3\}$. Accordingly, the weightfactor (3.9) can assume only three different values F_k , $k \in \{1, 2, 3\}$ which are given by (2.13). The limit (3.4) can now be written as

$$Z_{\text{SOS}}^N = \sum_{I \in \mathcal{I}_N} \omega_c(I). \tag{3.10}$$

The ‘return to the origin’ condition $h_N = 0$ for the interface can be relaxed. Let indeed \tilde{I}_N be the set of SOS-interfaces of width N constructed in the same way as above, but with the condition $h_N = 0$ removed. Let furthermore

$$\tilde{Z}_{\text{SOS}}^N = \sum_{I \in \tilde{I}_N} \omega_c(I) \tag{3.11}$$

be the corresponding partition function. It can then be shown by standard arguments (see, e.g., [19, 4]) that

$$\lim_{N \rightarrow +\infty} \frac{1}{2N+1} \ln(Z_{\text{SOS}}^N) = \lim_{N \rightarrow +\infty} \frac{1}{2N+1} \ln(\tilde{Z}_{\text{SOS}}^N). \tag{3.12}$$

We will thus consider the partition function \tilde{Z}_{SOS}^N rather than Z_{SOS}^N in the following.

3.2. Gallavotti jumps

Let I be an interface of width N , $\mathcal{H} = \{h_i\}_{i \in \{-N, \dots, N\}}$ the associated collection of heights, and $V(I)$ the collection of vertical bonds belonging to I . $V(I)$ splits up into maximal connected components which we will call *Gallavotti jumps* hereafter. We introduce the *height difference* X_i between line $i + 1$ and i by $X_i \equiv h_{i+1} - h_i$ for each $i \in \{-N, \dots, N - 1\}$, and let $J(I) \equiv \{X_{-N}, \dots, X_{N-1}\}$. Whenever $X_i \neq 0, i \in \{-N, \dots, N - 1\}$, we denote the corresponding jump by \tilde{X}_i . In this case X_i will also be called a jump since there is a one-to-one correspondence between jumps and nonzero height differences ($|X_i|$ equals indeed the number of bonds contained in \tilde{X}_i). We will use these notions interchangeably in the following. We also introduce the collection $\Sigma(I) \equiv \{s_{-N}, \dots, s_{N-1}\}$ of variables called *signs* defined for each $i \in \{-N, \dots, N - 1\}$ by

$$s_i \equiv \begin{cases} +1 & \text{if } X_i > 0 \\ 0 & \text{if } X_i = 0 \\ -1 & \text{if } X_i < 0. \end{cases}$$

The collection $\Sigma(I)$ will be called *signature of the interface* I hereafter. The set of all signatures corresponding to some interface of width N can be identified with \mathcal{Q}^{2N} , where $\mathcal{Q} \equiv \{-1, 0, 1\}$.

We say that two neighbouring jumps X_i and X_{i+1} (resp. two neighbouring signs s_i and s_{i+1}) form a *peak* p of $J(I)$ (resp. a *peak* \tilde{p} of the signature $\Sigma(I)$), iff $s_i = +1$ and $s_{i+1} = -1$. The set of all peaks of $J(I)$ (resp. $\Sigma(I)$) will be denoted by $\mathcal{P}(I)$ (resp. $\mathcal{P}(\Sigma(I))$). If a jump $X \in J(I)$ (resp. a nonzero sign s) is not part of a peak of $J(I)$ (resp. a peak of $\Sigma(I)$), we call it *isolated*. The set of all isolated jumps (resp. signs) belonging to $J(I)$ (resp. $\Sigma(I)$) will be denoted by $\mathcal{J}(I)$ (resp. $\mathcal{J}(\Sigma(I))$). We say moreover that a site $x \in S(I)$ is the *neighbour* of a jump \tilde{X} , iff $|E^*(x) \cap \tilde{X}| \neq \emptyset$, and we write $x \sim \tilde{X}$. The *neighbourhood* of a jump $X \in J(I)$ is then defined to be the set $\mathcal{N}(X) \equiv \{x \in S(I) | x \sim \tilde{X}\}$. Only jumps belonging to the same peak have intersecting neighbourhoods. More generally, if A is an arbitrary collection of jumps, we define its neighbourhood $\mathcal{N}(A) \equiv \cup_{X \in A} \mathcal{N}(X)$. Let $\mathcal{R} \equiv S(I) \setminus \mathcal{N}(J(I))$. By definition, the collection $\{\mathcal{R}, \mathcal{N}(X), \mathcal{N}(p)\}_{X \in \mathcal{J}(I), p \in \mathcal{P}(I)}$ forms a partition of $S(I)$. Thus, if we define for any set of sites $A \subset S(I)$ the function $\bar{f}(A) \equiv \prod_{x \in A} f(x)$, where f is given by (3.9), the weightfactor (3.8) reads

$$\omega_c(I) = \bar{f}(\mathcal{R}) \prod_{X \in \mathcal{J}(I)} \bar{f}(\mathcal{N}(X)) \prod_{p \in \mathcal{P}(I)} \bar{f}(\mathcal{N}(p)). \tag{3.13}$$

Basic geometric observations lead moreover to the following results (see figure 2 for more insight):

- any site belonging to \mathcal{R} is of type 1;

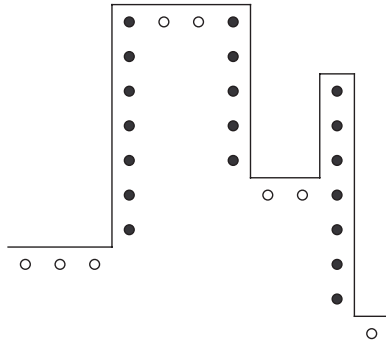


Figure 2. An interface I (solid line) exhibiting two isolated jumps on the left and a single peak on the right. The corresponding neighbourhoods are indicated by the black dots. The remaining part of $S(I)$ corresponds to the set \mathcal{R} (white dots).

- if X is an arbitrary isolated jump, then $\mathcal{N}(X)$ contains exactly one site of type 2 and $|X| - 1$ sites of type 1,
- if $p = (X, X')$ is an arbitrary peak, then $\mathcal{N}(p)$ contains exactly one site of type 3, $\min(|X|, |X'|) - 1$ sites of type 2, and $\max(|X|, |X'|) - \min(|X|, |X'|)$ sites of type 1.

Taking the latter observations into account, equation (3.13) takes the more explicit form

$$\omega_c(I) = F_1^{(2N+1)} \prod_{X_j \in \mathcal{J}(I)} F_2 F_1^{|X_j|-2} \times \prod_{p=(X_i, X_{i+1}) \in \mathcal{P}(I)} F_3 F_2^{\min(|X_i|, |X_{i+1}|-1)} F_1^{\max(|X_i|, |X_{i+1}|-1) - \min(|X_i|, |X_{i+1}|-1)} \tag{3.14}$$

where F_1, F_2 and F_3 are given by (2.13), and one has used the fact that the number of isolated jumps, peaks and sites belonging to \mathcal{R} necessarily add up to $2N + 1$. Now let $\Sigma = \{s_{-N}, \dots, s_{N-1}\} \in \mathcal{Q}^{2N}$ be a given signature, and let $\omega_{\text{red}}(\Sigma)$ be the reduced weight-factor defined by

$$\omega_{\text{red}}(\Sigma) \equiv \sum_{I \in \tilde{\mathcal{I}}_N : \Sigma(I) = \Sigma} \omega_c(I) \tag{3.15}$$

where the sum is over all interfaces having the same signature Σ . Then

$$\tilde{Z}_{\text{SOS}}^N = \sum_{\Sigma \in \mathcal{Q}^{2N}} \omega_{\text{red}}(\Sigma). \tag{3.16}$$

Let us recall that $F_3 < F_2 < F_1 < 1$. If one introduces numbers A and B defined by

$$A \equiv F_2 \sum_{|X_j| \geq 1} F_1^{|X_j|-2} = \frac{F_2 F_1^{-1}}{1 - F_1} \tag{3.17}$$

and

$$B \equiv F_3 \sum_{|X_i| \geq 1} \sum_{|X_{i+1}| \geq 1} F_2^{\min(|X_i|, |X_{i+1}|-1)} F_1^{\max(|X_i|, |X_{i+1}|-1) - \min(|X_i|, |X_{i+1}|-1)} \\ = F_3 \sum_{n \geq 1} F_2^{n-1} F_1^{-1} + 2F_3 \left\{ \sum_{|X_{i+1}| > |X_i| \geq 1} F_2^{|X_i|-1} F_1^{|X_{i+1}|-|X_i|-1} \right\}$$

$$\begin{aligned} &= \frac{F_3 F_1^{-1}}{1 - F_2} + 2F_3 \left\{ \sum_{|X_{i+1}| \geq 2} \sum_{|X_i|=1}^{|X_{i+1}|-1} (F_2 F_1^{-1})^{|X_i|-1} F_1^{|X_{i+1}|-2} \right\} \\ &= \frac{F_3 F_1^{-1}}{1 - F_2} + 2F_3 \left\{ \sum_{|X_{i+1}| \geq 2} \left(\frac{1 - (F_2 F_1^{-1})^{|X_{i+1}|-1}}{1 - F_2 F_1^{-1}} \right) F_1^{|X_{i+1}|-2} \right\} \\ &= \frac{F_3 F_1^{-1}}{1 - F_2} + \frac{2F_3}{1 - F_2 F_1^{-1}} \left\{ \frac{1}{1 - F_1} - \frac{F_2 F_1^{-1}}{1 - F_2} \right\} = \frac{F_3(1 + F_1^{-1})}{(1 - F_1)(1 - F_2)} \end{aligned}$$

a straightforward calculation starting from (3.14) shows that $\omega_{\text{red}}(\Sigma)$ reads

$$\omega_{\text{red}}(\Sigma) = F_1^{(2N+1)} A^{|\mathcal{J}(\Sigma)|} B^{|\mathcal{P}(\Sigma)|}. \tag{3.18}$$

3.3. A one-dimensional model

We now note that

$$|\mathcal{P}(\Sigma)| = \sum_{i=-N}^{N-1} \delta(s_i, +1) \delta(s_{i+1}, -1) \tag{3.19}$$

and

$$|\mathcal{J}(\Sigma)| = \sum_{i=-N}^{N-1} (1 - \delta(s_i, 0)) - 2 \sum_{i=-N}^{N-1} \delta(s_i, +1) \delta(s_{i+1}, -1). \tag{3.20}$$

Defining the two real-valued parameters,

$$\begin{cases} h \equiv \ln(A) \\ \gamma \equiv \ln(B) - 2 \ln(A), \end{cases} \tag{3.21}$$

we can thus write expression (3.18) under the more convenient form

$$\omega_{\text{red}}(\Sigma) = F_1^{(2N+1)} \exp \left\{ \sum_{i=-N}^{N-1} \gamma \delta(s_i, +1) \delta(s_{i+1}, -1) + \sum_{i=-N}^{N-1} h(1 - \delta(s_i, 0)) \right\}. \tag{3.22}$$

By (3.16), the two-dimensional SOS-model is thus equivalent to a one-dimensional three-state model with external magnetic field h and a nearest-neighbour interaction of strength γ . The random-variables s_i take values in the set $\mathcal{Q} \equiv \{-1, 0, +1\}$, and the Boltzmann weight of a given configuration $\Sigma \in \mathcal{Q}^{2N}$ is (up to normalization) given by (3.22). We can now derive an exact formula for the free energy density of this model by using the transfer-matrix method. Let

$$M(\gamma, h) \equiv \begin{pmatrix} e^h & e^{\frac{h}{2}} & e^h \\ e^{\frac{h}{2}} & 1 & e^{\frac{h}{2}} \\ e^{\gamma+h} & e^{\frac{h}{2}} & e^h \end{pmatrix}.$$

Then the partition function of the composite SOS-model can be written as

$$\tilde{Z}_{\text{SOS}}^N = F_1^{(2N+1)} \text{Tr}(M(\gamma, h)^{2N-1} M(0, h)). \tag{3.23}$$

Where Tr denotes the trace operation, and γ and h are given by (3.21). The characteristic polynomial of $M(\gamma, h)$

$$P(\lambda) = -\lambda(\lambda^2 - (1 + 2e^h)\lambda + e^{2h}(1 - e^\gamma))$$

has two nonzero real roots given by

$$\lambda_{\pm} \equiv \frac{2e^h + 1}{2} \left\{ 1 \pm \sqrt{1 + \frac{4(e^h - 1)}{(2 + e^{-h})^2}} \right\}.$$

Performing the relevant base change, we can thus cast $M(\gamma, h)$ in a diagonal form

$$\tilde{M}(\gamma, h) = \begin{pmatrix} \lambda_+ & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \lambda_- \end{pmatrix}. \quad (3.24)$$

Since λ_+ is the greatest eigenvalue of $M(\gamma, h)$, we then conclude by (2.11), (3.12), (3.23) and (3.24)

$$\tau_{12} = \lim_{N \rightarrow +\infty} -\frac{1}{\beta(2N+1)} \ln(F_1^{(2N+1)} \text{Tr}(\tilde{M}^{(2N+1)})) = -\frac{1}{\beta} (\ln(F_1) + \ln(\lambda_+)).$$

That is, in terms of F_1 , F_2 and F_3 ,

$$\begin{aligned} \tau_{12} = -\frac{1}{\beta} & \left\{ \ln\left(\frac{F_2}{2(1-F_1)}\right) \right. \\ & \left. + \ln\left(2 + \frac{1-F_1}{F_2 F_1^{-1}} + \sqrt{\left(2 + \frac{1-F_1}{F_2 F_1^{-1}}\right)^2 + 4\left(\frac{F_3 F_2^{-2} F_1 (1-F_1^2)}{1-F_2} - 1\right)}\right) \right\}. \end{aligned} \quad (3.25)$$

4. Concluding remarks

Let us first compare the exact expression (3.25) with known results. Remember from (2.9) and (2.12) that the concentration of the species $i \in \{1, 2\}$ is given by $c_i = e^{\mu_i}$. If we allow only particles of type 1 in the mixture (i.e. if we set $c_2 = 0$) then (3.25) should give us the surface tension τ_1 of species 1. In that case $F_k = e^{-k\beta J_1}$, $k \in \{1, 2, 3\}$, and the latter expression reduces as we expect it to the well-known formula:

$$\tau_1 = J_1 + \frac{1}{\beta} \ln\left(\tanh\left(\frac{\beta J_1}{2}\right)\right), \quad (4.1)$$

giving the free energy density of a one-component SOS-model [27]. It is an increasing function of J_1 which goes continuously from $-\infty$ to $+\infty$. Similarly, the surface tension τ_2 of species 2 is shown to obey the same law with J_1 replaced by J_2 . Also, if the two individual surface tensions coincide, one has $\tau_{12} = \tau_1 = \tau_2$ as one should.

In the low temperature regime (i.e. for large β), (3.25) reads

$$\tau_{12} = -\frac{1}{\beta} \left\{ \ln(F_1) + 2\frac{F_2}{F_1} + o\left(\frac{F_2}{F_1}\right) \right\} \quad (4.2)$$

where one has used the facts that

$$\lim_{\beta \rightarrow +\infty} F_1 = \lim_{\beta \rightarrow +\infty} F_2 = \lim_{\beta \rightarrow +\infty} F_3 = \lim_{\beta \rightarrow +\infty} \frac{F_2}{F_1} = \lim_{\beta \rightarrow +\infty} \frac{F_3}{F_1} = \lim_{\beta \rightarrow +\infty} \frac{F_3}{F_2} = 0. \quad (4.3)$$

The next-to-leading-order term in expansion (4.2) is in perfect agreement with the low temperature results obtained in [8].

The leading-order term (i.e. $-\frac{1}{\beta} \ln(F_1)$) corresponds to the contribution of the flat interface to the surface tension. Since at low temperatures one has from (4.1) $\tau_i \approx J_i$ for $i = 1, 2$,

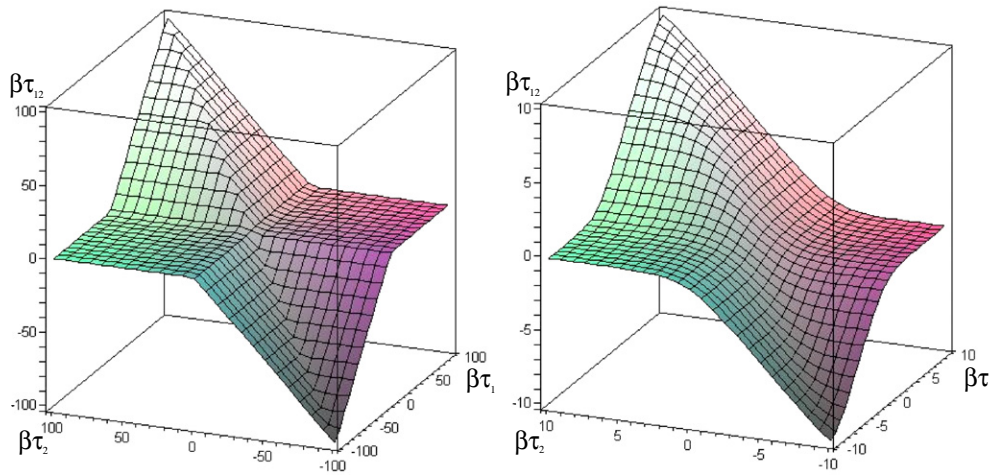


Figure 3. The surface tension τ_{12} of the binary mixture as a function of the individual surface tensions τ_1 and τ_2 . The concentration of species 1 has been set to 0.3, and the axes have been scaled by the inverse temperature β . The plot on the right-hand side shows the region around $(0, 0)$ in more detail.

it moreover coincides with Guggenheim’s formula (1.1) which thus appears to be a good approximation of the exact formula at low temperatures.

One might as well like to have a look at the plot of the surface tension of the mixture as a function of the individual surface tensions to gain some more qualitative insight. Expression (4.1) can indeed be inverted to yield

$$e^{\beta J_1} = \frac{1}{2}(e^{\beta\tau_1} + 1 + \sqrt{e^{2\beta\tau_1} + 6e^{\beta\tau_1} - 1}). \tag{4.4}$$

So that (3.25) provides a formula for the surface tension of the mixture which depends only on $\beta\tau_1, \beta\tau_2$ and the concentrations c_1 and c_2 . For a fixed concentration c_1 , the typical behaviour of τ_{12} as a function of τ_1 and τ_2 is shown in figure 3.

Together with the results

$$f(c_1) \equiv \lim_{\tau_2 \rightarrow +\infty} \lim_{\tau_1 \rightarrow -\infty} \tau_{12} = \ln\left(\frac{2c_2}{c_1}\right) - \ln\left(2 + c_2 + \sqrt{c_2^2 + 8}\right) \tag{4.5}$$

$$f(c_2) \equiv \lim_{\tau_2 \rightarrow -\infty} \lim_{\tau_1 \rightarrow +\infty} \tau_{12} = \ln\left(\frac{2c_1}{c_2}\right) - \ln\left(2 + c_1 + \sqrt{c_1^2 + 8}\right) \tag{4.6}$$

$$\lim_{\tau_2 \rightarrow +\infty} \left\{ \left(\lim_{\tau_1 \rightarrow +\infty} \tau_{12} \right) - \tau_2 \right\} = \ln\left(\frac{1}{c_2}\right) \tag{4.7}$$

$$\lim_{\tau_2 \rightarrow -\infty} \left\{ \left(\lim_{\tau_1 \rightarrow -\infty} \tau_{12} \right) - \tau_2 \right\} = \ln(c_2), \tag{4.8}$$

the plot suggests that the typical behaviour of the surface tension τ_{12} of the mixture is roughly as follows when the concentration c_1 is not too close to zero or one.

If $\tau_1 > 0$ and $\tau_2 > 0$ one has $\tau_{12} \approx \min\{\tau_1, \tau_2\}$, if $\tau_1 < 0$ and $\tau_2 < 0$ one has $\tau_{12} \approx \max\{\tau_1, \tau_2\}$, if $\tau_1 < 0$ and $\tau_2 > 0$ one has $\tau_{12} \approx f(c_1)$, if $\tau_1 > 0$ and $\tau_2 < 0$ one has $\tau_{12} \approx f(c_2)$. Significant deviations from this qualitative behaviour are seen only when c_1

is close enough to one or zero, in which case one continuously recovers the trivial relations $\tau_{12} = \tau_1$ (resp. $\tau_{12} = \tau_2$). Although the physicality of negative surface tensions is still a matter of debate [1, 2, 16], we draw the reader's attention to the behaviour of τ_{12} when τ_1 and/or τ_2 are negative, which does not correspond to what one would intuitively expect at first sight. The behaviour of τ_{12} in the region $\tau_1, \tau_2 > 0$ in turn is easily understood: in this regime the entropy has only little influence, and the component with the lower surface energy tends to be near the interface.

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