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On the Statistical Mechanics and Surface Tensions of Binary Mixtures

J. De Coninck,[1] S. Miracle–Solé,[2] and J. Ruiz[2]

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Within a lattice model describing a binary mixture with fixed concentrations of the species we discuss the relationship between the surface tension of the mixture and the concentrations.

KEY WORDS: Surface tensions; binary mixtures; interfaces.

1. INTRODUCTION

The notion of surface tension, or interfacial free energy per unit area, plays a key role in many studies concerning the surface phenomena and the phase coexistence.

When we consider a solid or a fluid, which is a mixture of two chemical species 1 and 2, in equilibrium with its vapor, one of the problems, experimentally as well as theoretically, is to determine how the corresponding surface tension depends on the composition of the mixture.

Some relationship is expected which would give this surface tension, here denoted $\tau_{(1,2)|0}$, as an interpolation between the two surface tensions, $\tau_{1|0}$ and $\tau_{2|0}$, of each of the species when they are chemically pure.

Using thermodynamical considerations several equations have been derived in the literature, according to different assumptions.

Thus, for ideal or nearly ideal solutions, a fairly simple treatment, due to Guggenheim,[(1)] leads to the following equation

$$e^{-\beta a^2 \tau_{(1,2)|0}} = c_1 e^{-\beta a^2 \tau_{1|0}} + c_2 e^{-\beta a \tau_{2|0}}, \tag{1.1}$$

[1]Centre de Recherche en Modélisation Moléculaire, Université de Mons–Hainaut, 20 place du Parc, B-7000, Mons, Belgium; e-mail: Joel.De.Coninck@galileo.umh.ac.be
[2]Centre de Physique Théorique, CNRS, Luminy case 907, F-13288 Marseille Cedex 9, France; e-mail: Salvador.Miracle-Sole, Jean.Ruiz@cpt.univ-mrs.fr

where c_1 is the fixed molar fraction of species 1 in the $(1,2)$ mixture, $c_2 = 1 - c_1$, the fixed molar fraction of species 2, a^2 is the mean surface area per molecule, and $\beta = 1/kT$ is the inverse temperature.

A very simple relationship for the so-called regular solutions comes from Defay and Prigogine,[2] who proposed the equation

$$\tau_{(1,2)|0} = c_1 \tau_{1|0} + c_2 \tau_{2|0} - K c_1 c_2 \tag{1.2}$$

with K a semiempirical constant.

A simple treatment due to Eberhart[3] assumes that the surface tension of a binary solution is linear in the surface composition, that is

$$\tau_{(1,2)|0} = c_1^s \tau_{1|0} + c_2^s \tau_{2|0}, \tag{1.3}$$

where the c_i^s, $i = 1, 2$, denote the mole fraction near the surface of phase separation, and that the ratio c_1^s/c_1 is proportional to the ratio c_2^s/c_2.

Finally, when the surface tensions $\tau_{1|0}$ and $\tau_{2|0}$ differ appreciably, a semiempirical equation attributed to Szyszkowsky[4,5] gives:

$$\frac{\tau_{(1,2)|0}}{\tau_{1|0}} = 1 - B \ln\left(1 + \frac{c_2}{A}\right), \tag{1.4}$$

where two characteristic constants A and B of the compounds have been used, and c_2 is the concentration of the species with the smaller surface tension.

We refer the reader to Adamson's book[6] (Chapter III, Section 4), and references therein, for a detailed discussion of the above equations. On the other hand, an extensive development for various types of nonideal solutions that has been made by Defay *et al.*,[7] can be found in their monography.

More recently, an interface model with a two-valued random interaction was introduced by two of the present authors in ref. 8 to describe the phase boundary from a microscopic point of view. The surface tension for that model could be computed according to a quenched or annealed disorder and one obtains

$$\begin{aligned} \tau_{(1,2),0}^{\text{quenched}} &= c_1 \tau_{1,0} + c_2 \tau_{2,0}, \\ e^{-\beta \tau_{(1,2)|0}^{\text{annealed}}} &= c_1 e^{-\beta \tau_{1,0}} + c_2 e^{-\beta \tau_{2,0}} \end{aligned}$$

in agreement with the above Eq. (1.1) or (1.3).

The aim of the present paper is to discuss the problem within a lattice bulk statistical mechanical model describing the binary mixture in equilibrium with its vapor. Previous studies of various models of binary lattice gases can be found in refs. 9 and 10.

Here, we consider a lattice gas system with two kinds of particles, where each lattice site can be in one of the three states, 0, 1, and 2, interpreted, respectively, as an empty site, a site occupied by a particle of the first kind of the model, and a site occupied by a particle of the second kind. Whenever the particles 2 are not allowed the system reduces to the usual Ising model, in its lattice gas version, with coupling constant $J_1/2$. We consider the system in the phase coexistence region and denote by $\tau_{1|0}$ the corresponding surface tension between the dense and the dilute phases. Analogously, when particles 1 are not allowed, it reduces to the Ising model with coupling constant $J_2/2$ and we let $\tau_{2|0}$ be the corresponding surface tension.

We can also study our three state model in the phase coexistence region (with the help of Pirogov Sinai theory) and then interpret the dense phase as the binary mixture, the dilute phase as the corresponding vapor, and $\tau_{(1,2)|0}$ as the surface tension between these two phases. On the other hand the concentration of particles 1 and 2 in the dense phase can be fixed to take any given values.

As a main result of this paper we prove that, at low temperatures, the following equation holds, for the surface tension of our model

$$e^{-\beta(\tau_{(1,2)|0}-\mathcal{F})} = c_1^* e^{-\beta(\tau_{1|0}-\mathcal{F}_1)} + c_2^* e^{-\beta(\tau_{2|0}-\mathcal{F}_2)}. \tag{1.5}$$

Here $\mathcal{F}_i$, $(i = 1, 2)$ is the specific free energy of the gas of "jumps" describing the Gallavotti's line of phase separation for the Ising model in two-dimensions,[11] and that of the gas of the "walls" describing the Dobrushin's microscopic interface[12] in three-dimensions. This means that $\tau_{1|0} - \mathcal{F}_1 = J_1$ and $\tau_{2|0} - \mathcal{F}_2 = J_2$ are the respective energy costs per unit length or unit area of the $1|0$ and the $2|0$ interfaces. The quantity $\mathcal{F}$ is the specific free energy (which can be expressed as a convergent series at low temperatures) of a gas of some geometrical objects called aggregates. In dimension $d = 2$, those aggregates are the natural generalizations to our model of the jumps of Gallavotti's line and the leading term of the series giving this free energy $\mathcal{F}$ is

$$-\frac{2}{\beta}\frac{c_1^* e^{-2\beta J_1} + c_2^* e^{-2\beta J_2}}{c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2}}.$$

In dimension $d=3$, they are the natural generalizations of the walls of the Dobrushin's interface and then the leading term of the series is

$$-\frac{1}{\beta}\frac{c_1^* e^{-5\beta J_1}+c_2^* e^{-5\beta J_2}}{c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2}}-\frac{1}{\beta}\frac{(c_1^* e^{-2\beta J_1}+c_2^* e^{-2\beta J_2})^4}{(c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2})^4}.$$

The coefficients c_1^* and c_2^* are related to the concentrations c_1 and c_2 of the particles 1 and the particles 2 through Eq. (5.7). This equation gives at low temperatures:

$$\begin{aligned} c_i^* = c_i\Big[& 1-\left(c_1 e^{-\beta J_1}+c_2 e^{-\beta J_2}\right)^{2d} - 2d c_i e^{-\beta J_i}\left(c_1 e^{-\beta J_1}+c_2 e^{-\beta J_2}\right)^{2d-1} \\ & -2(d+1)c_i\left(c_1 e^{-\beta J_1}+c_2 e^{-\beta J_2}\right)^{2d}+O\left(e^{-(2d+1)\beta\min\{J_1,J_2\}}\right)\Big] \end{aligned} \tag{1.6}$$

for $i=1,2$.

The paper is organized as follows. The model is defined in Section 2 which also provides the analysis of the ground states of the system. Section 3 is devoted to the study of the Gibbs states of the system at low temperatures and of the coexistence between the mixture and the vapor. Section 4 contains the definitions of the surface tensions and an expansion of the surface tension between the mixture and the vapor in terms of interfaces. Section 5 contains the presentation of the relationship between surface tensions. The proofs are given in Sections 6 and 7.

2. THE MODEL

We consider a cubic lattice $\mathbb{Z}^d$, of dimension $d=2,3$, and to each site $\mathbb{Z}^d$ we associate a variable s_x which taking values in the set $\Omega=\{0,1,2\}$ specifies one of the possible three states of the system at each lattice site. We say that the site x is empty if $s_x=0$ and that is occupied by a particle of kind 1 or of kind 2 if $s_x=1$ or 2. The following Hamiltonian

$$H=-\sum_{\langle x,y\rangle}\sum_{\alpha=0}^{2}\sum_{\beta=0}^{2}E_{\alpha\beta}\,\delta(s_x,\alpha)\delta(s_y,\beta), \tag{2.1}$$

where $\langle x,y\rangle$ denote nearest–neighbor pairs, δ is the usual Kronecker symbol, $\delta(s,s')=1$ if $s=s'$ and $\delta(s,s')=0$ otherwise, and $E_{\alpha\beta}=E_{\beta\alpha}$ are the coupling constants, is of the form of the Blume–Emery–Griffiths model[13] which describes a general three state lattice system for the case of nearest–neighbor interactions. We shall assume here that

$$2E_{12} = E_{11} + E_{22} \tag{2.2}$$

in order to ensure that particles of kinds 1 and 2 could be mixed arbitrarily without any cost of energy. When these identities are not satisfied two new thermodynamic phases, either rich in particles of kind 1 or in particles of kind 2, may appear as equilibrium states of the system.

With the assumption of hypothesis (2.2) the general Hamiltonian (2.1) can be reduced to the form

$$\begin{aligned} H = \sum_{\langle x,y\rangle} \Big[& J_1\big(\delta(s_x,1)\delta(s_y,0) + \delta(s_x,0)\delta(s_y,1)\big) \\ & + J_2\big(\delta(s_x,2)\delta(s_y,0) + \delta(s_x,0)\delta(s_y,2)\big)\Big] \end{aligned} \tag{2.3}$$

that is, the case in which the coupling constants satisfy $E_{10} = E_{01} = -J_1$, $E_{20} = E_{02} = -J_2$ and $E_{\alpha\beta} = 0$ otherwise. Furthermore, we assume that J_1 and J_2 are positive constants.

In order to see this fact we consider, as it is often convenient, the reformulation of the three state lattice system in the language of a magnetic system of spin one. To do so, we define the spin variable σ_x at the x site via

$$\begin{aligned} \delta(s_x,0) &= 1 - \sigma_x^2, \\ \delta(s_x,1) &= \sigma_x(\sigma_x + 1)/2, \\ \delta(s_x,2) &= \sigma_x(\sigma_x - 1)/2 \end{aligned} \tag{2.4}$$

so that $\sigma_x = 0, 1, -1$ corresponds to the presence at site x of the state $0, 1$ or 2, respectively. In terms of the spins, the general Hamiltonian (2.1) takes the form

$$\begin{aligned} H = & \sum_{\langle x,y\rangle} \mathcal{J}(\sigma_x - \sigma_y)^2 - \mathcal{K}\sigma_x^2\sigma_y^2 - \mathcal{C}(\sigma_x\sigma_y^2 + \sigma_x^2\sigma_y) \\ & - \sum_x (\mathcal{A}\sigma_x + \mathcal{B}\sigma_x^2). \end{aligned} \tag{2.5}$$

The pair interactions of the system are given by

$$\begin{aligned} E_{11}+E_{22}-2E_{12} &= 8\mathcal{J}, \\ E_{11}+E_{00}-2E_{01} &= 2\mathcal{J}+\mathcal{K}+2\mathcal{C}, \\ E_{22}+E_{00}-2E_{02} &= 2\mathcal{J}+\mathcal{K}-2\mathcal{C}. \end{aligned} \tag{2.6}$$

The last two terms can be treated as chemical potentials, with

$$\mathcal{A}=d(E_{01}-E_{02}) \text{ and } \mathcal{B}=d(E_{01}+E_{02}-2E_{00}-2\mathcal{J}).$$

We see that our hypothesis (2.2) implies

$$\mathcal{J}=0. \tag{2.7}$$

On the other hand, taking into account that

$$\begin{aligned} 2\delta(\sigma_x,1)\delta(\sigma_y,0) &= \sigma_x(\sigma_x+1)(1-\sigma_y^2)=\sigma_x^2+\sigma_x-\sigma_x\sigma_y^2-\sigma_x^2\sigma_y^2, \\ 2\delta(\sigma_x,-1)\delta(\sigma_y,0) &= \sigma_x(\sigma_x-1)(1-\sigma_y^2)=\sigma_x^2-\sigma_x+\sigma_x\sigma_y^2-\sigma_x^2\sigma_y^2, \end{aligned}$$

we obtain Hamiltonian (2.3), plus chemical potential terms, with

$$2J_1=K+2C, \quad 2J_2=K-2C. \tag{2.8}$$

We notice that condition (2.7) excludes the models discussed in the above mentioned refs. 9 and 10. In ref. 10, Lebowitz and Gallavotti have considered the cases $2\mathcal{J}=-\mathcal{K}>0$, $\mathcal{C}=0$, also studied by Wheeler and Widom,[9] and $\mathcal{J}>0$, $\mathcal{K}=\mathcal{C}=0$, usually known as the Blume–Capel model. They prove then the appearance at low temperatures of two phases, respectively reach in particles of kind 1 or of kind 2. When the two phases coexist one has, as a consequence of the condition $\mathcal{C}=0$, the equality between the two surface tensions $\tau_{1|0}$ and $\tau_{2|0}$. These models, therefore, would not be appropriate for the present study. The case $\mathcal{C}\neq 0$ (and $\mathcal{J}>0$) will be briefly commented in Section 5.

Let us now return to the discussion of Hamiltonian (2.3). Fixed densities of the three species are introduced through the canonical Gibbs ensemble of configurations $\mathbf{s}_\Lambda=\{s_x\}_{x\in\Lambda}$ in a finite box $\Lambda\subset\mathbb{Z}^d$, such that

$$\sum_{x\in\Lambda}\delta(s_x,0)=N_0, \quad \sum_{x\in\Lambda}\delta(s_x,1)=N_1 \quad \text{and} \quad \sum_{x\in\Lambda}\delta(s_x,2)=N_2. \tag{2.9}$$

Here N_0, N_1 and N_2 are nonnegative integers satisfying $N_0+N_1+N_2=|\Lambda|$ where $|\Lambda|$ denotes the number of sites of Λ. The associated partition functions with boundary condition bc are given by

$$Z_{\mathrm{bc}}(\Lambda; N_1, N_2) = \sum_{\mathbf{s}_\Lambda \in \Omega^\Lambda} e^{-\beta H_\Lambda(\mathbf{s}_\Lambda)} \delta\left(\sum_{x\in\Lambda} \delta(s_x, 1), N_1\right) \times \delta\left(\sum_{x\in\Lambda} \delta(s_x, 2), N_2\right) \chi^{\mathrm{bc}}(\mathbf{s}_\Lambda), \tag{2.10}$$

where $H_\Lambda(\mathbf{s}_\Lambda)$ is the Hamiltonian (2.3) with the sum over nearest–neighbors pairs $\langle x, y\rangle \subset \Lambda$ and $\chi^{\mathrm{bc}}(\mathbf{s}_\Lambda)$ is a characteristic function standing for the boundary condition bc. We shall be interested in particular to the following boundary conditions:

- the empty boundary condition: $\chi^{\mathrm{emp}}(\mathbf{s}_\Lambda)=\prod_{x\in\partial\Lambda} \delta(s_x, 0)$;
- the mixture boundary condition: $\chi^{\mathrm{mixt}}(\mathbf{s}_\Lambda)=\prod_{x\in\partial\Lambda}(1-\delta(s_x, 0))$;
- the free boundary condition: $\chi^{\mathrm{fr}}(\mathbf{s}_\Lambda)=1$.

Hereafter, the boundary $\partial\Lambda$ of the box Λ is the set of sites of Λ that have a nearest–neighbor in $\Lambda^c=\mathbb{Z}^d \setminus \Lambda$.

We define the free energy per site corresponding to the above ensemble as a function of the densities ρ_1 and ρ_2 of the particles 1 and 2:

$$f(\rho_1, \rho_2)= \lim_{\Lambda\uparrow\mathbb{Z}^d} -\frac{1}{\beta|\Lambda|} \ln Z_{\mathrm{bc}}(\Lambda; [\rho_1|\Lambda|], [\rho_2|\Lambda|]), \tag{2.11}$$

where $[\cdot]$ denotes the integer part and the thermodynamic limit $\Lambda\uparrow\mathbb{Z}^d$ is taken in the van Hoove sense.[14]

We introduce also a grand canonical Gibbs ensemble, which is conjugate to the previous ensemble, and whose partition function, in the box Λ is given by

$$\Xi_{\mathrm{bc}}(\Lambda; \mu_1, \mu_2)= \sum_{\mathbf{s}_\Lambda \in\Omega^\Lambda} e^{-\beta H_\Lambda(\mathbf{s}_\Lambda)+\mu_1\sum_{x\in\Lambda}\delta(s_x,1)+\mu_2\sum_{x\in\Lambda}\delta(s_x,2)}, \tag{2.12}$$

where the real numbers μ_1 and μ_2 replace as thermodynamic parameters the densities ρ_1 and ρ_2. We define the corresponding specific free energy, the pressure, as the limit

$$p(\mu_1,\mu_2)=\lim_{\Lambda\uparrow\mathbb{Z}^d}\frac{1}{|\Lambda|}\ln\Xi_{\mathrm{bc}}(\Lambda;\mu_1,\mu_2). \tag{2.13}$$

The equivalence of the two above ensembles is expressed in the following theorem.

Theorem 1. Limits (2.11) and (2.13), which define the above free energies, exist. They are convex functions of their parameters and are related by the Legendre transformations

$$p(\mu_1,\mu_2) = \sup_{\rho_1,\rho_2}[\mu_1\rho_1+\mu_2\rho_2-\beta f(\rho_1,\rho_2)], \tag{2.14}$$

$$\beta f(\rho_1,\rho_2) = \sup_{\mu_1,\mu_2}[\mu_1\rho_1+\mu_2\rho_2-p(\mu_1,\mu_2)]. \tag{2.15}$$

Proof. We consider two parallelepipedic boxes Λ' and Λ'' of both the same size and paste them to form a parallelepipedic box $\Lambda=\Lambda'\cup\Lambda''$ in such a way that $\Lambda'\cap\Lambda''=\emptyset$ and each site of some side of Λ' is a nearest–neighbor of a site of a side of Λ''. It is easy to see that the following sub-additivity property holds:

$$Z_{\mathrm{emp}}(\Lambda;N_1'+N_1'',N_2'+N_2'')\geqslant Z_{\mathrm{emp}}(\Lambda';N_1',N_2')Z_{\mathrm{emp}}(\Lambda'';N_1'',N_2'').$$

The same property is shared by the partition function with mixt boundary conditions. Then the statements of the theorem follow from standard arguments in the theory of the thermodynamic limit.[14] ∎

We next introduce the finite volume Gibbs measures (a specification) associated with the second ensemble:

$$\mathbb{P}_\Lambda^{\mathrm{bc}}(\mathbf{s}_\Lambda)=\frac{e^{-\beta\tilde{H}_\Lambda(\mathbf{s}_\Lambda)}\chi^{\mathrm{bc}}(\mathbf{s}_\Lambda)}{\Xi_{\mathrm{bc}}(\Lambda;\mu_1,\mu_2)}, \tag{2.16}$$

where

$$\tilde{H}_\Lambda(\mathbf{s}_\Lambda)=H_\Lambda(\mathbf{s}_\Lambda)-\frac{\mu_1}{\beta}\sum_{x\in\Lambda}\delta(s_x,1)-\frac{\mu_2}{\beta}\sum_{x\in\Lambda}\delta(s_x,2). \tag{2.17}$$

They determine by the Dobrushin–Landford–Ruelle equations the set of Gibbs states $\mathcal{G}_\beta(\tilde{\mathcal{H}})$ on $\mathbb{Z}^d$ corresponding to the Hamiltonian $\tilde{H}$ at inverse temperature β (see ref. 15). If a Gibbs state $\mathbb{P}\in\mathcal{G}_\beta(\tilde{\mathcal{H}})$ happens to equal the limit $\lim_{\Lambda\uparrow\mathbb{Z}^d}\mathbb{P}^{\mathrm{bc}}_\Lambda(\cdot)$, we shall call it the Gibbs state with boundary condition bc.

In the zero temperature limit the Gibbs state with empty boundary condition is concentrated on the configuration with empty sites:

$$\lim_{\beta\to\infty}\mathbb{P}^{\mathrm{bc}}_\Lambda(\mathrm{emp}_\Lambda)=1, \tag{2.18}$$

where emp_Λ is the configuration where all the sites of Λ are empty, and this limit vanishes for any other configuration. Gibbs states at $\beta=\infty$ will be called ground states.

Let

$$R^{\mathrm{mixt}}_\Lambda=\left\{s\in\Omega^\Lambda:\forall x\in\Lambda,\,s_x\neq 0\right\} \tag{2.19}$$

be the *restricted ensemble* of configurations in Λ with non empty sites, and $R^{\mathrm{mixt}}_\Lambda(c)$, $0\leqslant c\leqslant 1$ the subset of configurations of $R^{\mathrm{mixt}}_\Lambda$ with exactly $[c|\Lambda|]=N$ sites occupied by a particle of the specie 1 (and $|\Lambda|-[c|\Lambda|]$ sites occupied by a particle of the specie 2). The number of configurations $R^{\mathrm{mixt}}_\Lambda(c)$ equals the binomial coefficient $\binom{|\Lambda|}{N}$.

With the mixture boundary conditions one has

$$\lim_{\beta\to\infty}\mathbb{P}^{\mathrm{mixt}}_\Lambda(\mathbf{s}_\Lambda)=\frac{e^{\mu_1[c|\Lambda|]}e^{\mu_2[(1-c)|\Lambda|]}}{(e^{\mu_1}+e^{\mu_2})^{|\Lambda|}}\quad\text{for each}\quad \mathbf{s}_\Lambda\in R^{\mathrm{mixt}}_\Lambda(c) \tag{2.20}$$

and

$$\lim_{\beta\to\infty}\mathbb{P}^{\mathrm{mixt}}_\Lambda(R^{\mathrm{mixt}}_\Lambda(c))=\frac{\binom{|\Lambda|}{N}e^{\mu_1 N}e^{\mu_2(|\Lambda|-N)}}{(e^{\mu_1}+e^{\mu_2})^{|\Lambda|}}, \tag{2.21}$$

while this limit vanishes for those $\mathbf{s}_\Lambda\notin R^{\mathrm{mixt}}_\Lambda$ (the denominator in (2.20) and (2.21) is the sum $\sum_{N=0}^{|\Lambda|}$ of the numerator of the R.H.S. of (2.21)). Notice that all configurations $\mathbf{s}_\Lambda\in R^{\mathrm{mixt}}_\Lambda(c)$ have the same probability. Moreover, by Stirling's approximation one has for large $|\Lambda|$ that $\binom{|\Lambda|}{[c|\Lambda|]}\approx\left[\left(\frac{1}{c}\right)^c\left(\frac{1}{1-c}\right)^{1-c}\right]^{|\Lambda|}$, and the maximum of $e^{\mu_1 c}/(e^{\mu_1}+e^{\mu_2})$ is reached for

$$c=\frac{e^{\mu_1}}{e^{\mu_1}+e^{\mu_2}}. \tag{2.22}$$

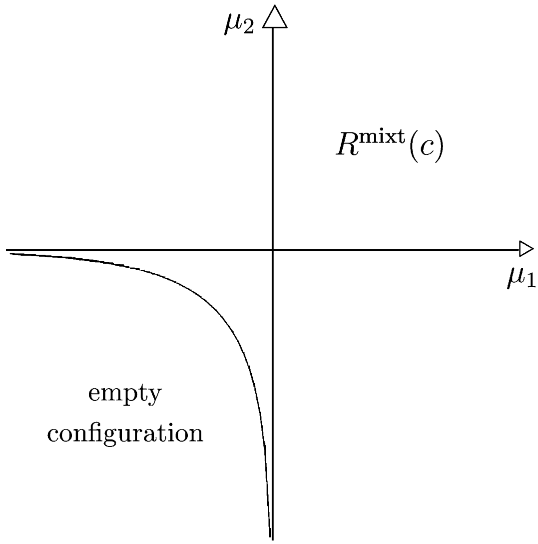

Fig. 1. The diagram of ground states.

The principle of maximal term gives that, for such values (2.21) tends to 1 in the thermodynamic limit. This means that the ground state with mixt boundary conditions is concentrated on the restricted ensemble $R^{\mathrm{mixt}}(c)$ of configurations of non empty sites with concentration c of particles 1 and concentration $1-c$ of particles 2.

With free boundary conditions, one has

$$\lim_{\beta\to\infty} \mathbb{P}^{\mathrm{fr}}_{\Lambda}(\mathrm{emp}_\Lambda) = \frac{1}{1+(e^{\mu_1}+e^{\mu_2})^{|\Lambda|}}, \tag{2.23}$$

$$\lim_{\beta\to\infty} \mathbb{P}^{\mathrm{fr}}_{\Lambda}(R^{\mathrm{mixt}}_{\Lambda}(c)) = \frac{\binom{|\Lambda|}{[c|\Lambda|]} e^{\mu_1|\Lambda|} e^{\mu_2[(1-c)|\Lambda|]}}{1+(e^{\mu_1}+e^{\mu_2})^{|\Lambda|}}, \tag{2.24}$$

Thus, with the above considerations, we get that for $e^{\mu_1}+e^{\mu_2}=1$, the configuration with empty sites coexists with the restricted ensemble $R^{\mathrm{mixt}}(c)$. The diagram of ground states is shown in Fig 1.

In the next section, we extend this analysis to low temperatures.

3. COEXISTENCE BETWEEN THE MIXTURE AND THE VAPOR

To extend the analysis of the previous section to the Gibbs states at low temperatures, we will express the partition functions (2.12) with empty and mixt boundary condition in term of contour models.

Let us first introduce the notions of contours by the following definitions.

Consider a configuration $\mathbf{s}_\Lambda$ with empty sites on the boundary $\partial\Lambda$ ($s_x = 0$ for all $x \in \partial\Lambda$). We define the boundary $B(\mathbf{s}_\Lambda)$ as the set of pairs $\{s_x, s_y\}$ such that $s_x \neq 0$ and $s_y = 0$. To a nearest–neighbor pair $\langle x, y\rangle$ let us associate

(a) in dimension 2, the unit bond (dual bond) b_{xy} that intersects the bond xy in its middle and orthogonal to xy;

(b) in dimension 3, the unit square (dual plaquette) p_{xy} that intersects the bond xy in its middle and orthogonal to xy.

Two pairs $\{s_x, s_y\}$ and $\{s_z, s_t\}$ of $B(\mathbf{s}_\Lambda)$ are said adjacent if one of the two conditions is fulfilled

(i) the dual bonds b_{xy} and b_{zt} (respectively, the plaquettes p_{xy} and p_{zt}) are connected;

(ii) $x = z$, $s_x = s_z \neq 0$, $s_y = s_t = 0$, and the bond xy with endpoints x and y is parallel to the bond with endpoints z and t.

A subset B of $B(\mathbf{s}_\Lambda)$ is called connected if the graph that joins all adjacent pairs of B is connected. It is called contour of the configuration $\mathbf{s}_\Lambda$ if it is a maximal connected component of $B(\mathbf{s}_\Lambda)$ (see Fig. 2).

0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	**0**	**0**	**0**	**0**	**0**	**0**	0	0	0	0	0	0	0
0	**0**	**2**	**1**	**2**	**1**	**2**	**2**	**0**	0	0	0	0	0	0
0	**0**	**1**	**0**	**0**	**0**	**0**	**2**	**0**	0	0	0	0	0	0
0	**0**	**1**	**0**	0	0	**0**	**2**	**0**	0	0	0	0	0	0
0	**0**	**2**	**0**	**0**	**0**	**0**	**1**	**0**	**0**	**0**	**0**	**0**	0	0
0	**0**	**1**	**2**	**1**	**2**	**1**	**2**	**0**	**1**	**2**	**1**	**2**	**0**	0
0	**0**	**1**	2	1	2	1	**2**	**0**	**2**	1	2	**1**	**0**	0
0	**0**	**2**	1	2	1	2	**1**	**0**	**1**	2	2	**2**	**0**	0
0	**0**	**1**	**1**	**2**	**1**	**2**	**1**	**0**	**2**	**1**	**2**	**1**	**0**	0
0	0	**0**	**0**	**0**	**0**	**0**	**0**	0	**0**	**0**	**0**	**0**	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Fig. 2. A configuration with two contours: the two rectangles on the left belong to the same contour due to the condition (ii) of adjacency.

The boundary and the contours of a configuration $\mathbf{s}_\Lambda$ with occupied sites on the boundary of Λ are defined in the same way.

A set Γ of pairs $\{s_x, s_y\}$ such that $s_x \neq 0$ and $s_y = 0$ is called contour if there exists a configuration $\mathbf{s}_\Lambda$ such that Γ is a contour of $\mathbf{s}_\Lambda$. We use $S_\alpha(\Gamma)$ to denote the set of sites for which $s_x = \alpha$. The set $\operatorname{supp}\Gamma = S_0(\Gamma) \cup S_1(\Gamma) \cup S_2(\Gamma)$ is called *support* of the contour Γ. We will also use $S(\Gamma) = S_1(\Gamma) \cup S_2(\Gamma)$ to denote the set of occupied sites of the contour, $L_1(\Gamma)$ (respectively, $L_2(\Gamma)$) to denote the number of nearest–neighbor pairs $\langle x, y\rangle$ such that $s_x = 1$ and $s_y = 0$ (respectively, $s_x = 2$ and $s_y = 0$) and $L(\Gamma) = L_1(\Gamma) + L_2(\Gamma)$.

Consider the configuration $\mathbf{s}_\Lambda$ having Γ as unique contour. The difference $\Lambda \setminus S(\Gamma)$ splits in components (set of sites for which the graph that joins all nearest–neighbor pairs is connected) with either all occupied sites or all empty sites. The component that contains $\partial\Lambda$, denoted $\operatorname{Ext}_\Lambda \Gamma$ is called *exterior* of the contour. When $\mathbf{s}_\Lambda$ has empty sites (respectively, occupied sites) on its boundary, Γ is called emp-contour (respectively, mixt-contour). The *interior* of the contour is the set $\operatorname{Int}\Gamma = \Lambda \setminus (S(\Gamma) \cup \operatorname{Ext}_\Lambda \Gamma)$. It is the union of the components of $\operatorname{Int}_{\mathrm{emp}} \Gamma$ with empty sites with the components of $\operatorname{Int}_{\mathrm{mixt}} \Gamma$ with occupied sites. Finally $V(\Gamma) = S(\Gamma) \cup \operatorname{Int}\Gamma$.

Two contours Γ_1 and Γ_2 are said compatible their union is not connected. They are mutually compatible external contours if furthermore $V(\Gamma_1) \subset \operatorname{Ext}_\Lambda \Gamma_2$ and $V(\Gamma_2) \subset \operatorname{Ext}_\Lambda \Gamma_1$.

With these definitions one gets the following expansions of the grand canonical partition functions

$$\Xi_{\mathrm{emp}}(\Lambda; \mu_1, \mu_2) = \sum_{\{\Gamma_1,\ldots,\Gamma_n\}_{\mathrm{ext}}} \prod_{i=1}^{n} \omega(\Gamma_i)\, \Xi_{\mathrm{emp}}(\operatorname{Int}_{\mathrm{emp}} \Gamma_i; \mu_1, \mu_2) \times \Xi_{\mathrm{mixt}}(\operatorname{Int}_{\mathrm{mixt}} \Gamma_i; \mu_1, \mu_2), \tag{3.1}$$

$$\Xi_{\mathrm{mixt}}(\Lambda, \mu_1, \mu_2) = \sum_{\{\Gamma_1,\ldots,\Gamma_n\}_{\mathrm{ext}}} (e^{\mu_1} + e^{\mu_2})^{|\Lambda \setminus \cup_{i=1}^{n} V(\Gamma_i)|} \times \prod_{i=1}^{n} \omega(\Gamma_i)\, \Xi_{\mathrm{emp}}(\operatorname{Int}_{\mathrm{emp}} \Gamma_i; \mu_1, \mu_2) \times \Xi_{\mathrm{mixt}}(\operatorname{Int}_{\mathrm{mixt}} \Gamma_i; \mu_1, \mu_2), \tag{3.2}$$

where the first sum is over families of mutually external emp–contours, the second sum is over families of mutually external mixt–contours, and

$$\omega(\Gamma) = e^{-\beta J_1 L_1(\Gamma) - \beta J_2 L_2(\Gamma) + \mu_1 |S_1(\Gamma)| + \mu_2 |S_2(\Gamma)|}. \tag{3.3}$$

We put

$$g_{\mathrm{emp}} = 0, \quad g_{\mathrm{mixt}} = \ln(e^{\mu_1} + e^{\mu_2}), \quad g_{\max} = \max\{g_{\mathrm{emp}}, g_{\mathrm{mixt}}\}. \tag{3.4}$$

We divide in (3.1) each Ξ_{mixt} by Ξ_{emp} and multiply it back again in the form (3.1). Continuing this process, and doing an equivalent procedure with (3.2), these relations lead to the following expansion for the partition functions with boundary condition $q = \mathrm{emp}$ or $q = \mathrm{mixt}$.

$$\Xi_q(\Lambda; \mu_1, \mu_2) = e^{g_q|\Lambda|} \sum_{\{\Gamma_1, \dots, \Gamma_n\}_{\mathrm{comp}}} \prod_{i=1}^{n} z_q(\Gamma_i), \tag{3.5}$$

where the sum is now over families of compatible q-contours and the activities $z_q(\Gamma)$ of contours are given by

$$z_q(\Gamma) = \omega(\Gamma) e^{-g_q|S(\Gamma)|} \frac{\Xi_m(\mathrm{Int}_m\ \Gamma; \mu_1, \mu_2)}{\Xi_q(\mathrm{Int}_q\ \Gamma; \mu_1, \mu_2)}, \tag{3.6}$$

where $m \neq q$.

The (generalized) Peierls estimates

$$\omega(\Gamma) e^{-g_{\max}|S(\Gamma)|} \leqslant e^{-\beta J L(\Gamma)}, \tag{3.7}$$

where $J = \min\{J_1, J_2\}$, allow us to have a good control of the behavior of our system at low enough temperatures using Pirogov–Sinai theory.[16] Choosing the Zahradnik's formulation of that theory,[17] we introduce to state our results, the following

Definition 1. For $q = \mathrm{emp}$ and $q = \mathrm{mixt}$ we define the truncated activity

$$z'_q(\Gamma) = \begin{cases} z_q(\Gamma) & \text{if } z_q(\Gamma) \leqslant e^{-\alpha L(\Gamma)}, \\ e^{-\alpha L(\Gamma)} & \text{otherwise,} \end{cases}$$

where α is some positive parameter to be chosen later (see Theorem 2).

Definition 2. The q–contour Γ is called stable if

$$z_q(\Gamma) \leqslant e^{-\alpha L(\Gamma)}, \tag{3.8}$$

i.e. if $z_q(\Gamma) = z'_q(\Gamma)$.

We define the truncated partition function $\Xi'_q(\Lambda)$ as the partition function obtained from (3.5) by leaving out unstable contours, namely

$$\Xi'_q(\Lambda; \mu_1, \mu_2) = e^{g_q|\Lambda|} \sum_{\{\Gamma_1,\dots,\Gamma_n\}_{\text{comp}}} \prod_{i=1}^{n} z'_q(\Gamma_i). \tag{3.9}$$

Here the sum goes over compatible families of *stable q–contours*. Let

$$p_q(\mu_1, \mu_2) = \lim_{\Lambda \uparrow \mathbb{Z}^d} \frac{1}{|\Lambda|} \ln \Xi'_q(\Lambda; \mu_1, \mu_2) \tag{3.10}$$

be the *meta-stable pressure* associated with the truncated partition function $\Xi'_q(\Lambda; \mu_1, \mu_2)$.

For α large enough the thermodynamic limit (3.10) can be controlled by a convergent cluster expansion.

Namely, to exponentiate the truncated partition function, we introduce multi-indexes X as functions from the set of contours into the set of nonnegative integers (see refs. 18 and 19). We let $\operatorname{supp} X = \cup_{\Gamma: X(\Gamma) \geqslant 1} \operatorname{supp} \Gamma$ and define the truncated functional

$$\Phi_q(X) = \frac{a(X)}{\prod_\Gamma X(\Gamma)!} \prod_\Gamma z_q(\Gamma)^{X(\Gamma)}, \tag{3.11}$$

where the factor $a(X)$ is a combinatoric factor defined in terms of the connectivity properties of the graph $G(X)$ with vertices corresponding to Γ with $X(\Gamma) \geqslant 1$ (there are $X(\Gamma)$ vertices for each such Γ) that are connected by an edge whenever the corresponding contours are incompatible). Namely, $a(X) = 0$ and hence $\Phi_q(X) = 0$ unless $G(X)$ is a connected graph in which case X is called a *cluster* and

$$a(X) = \sum_{G \subset G(X)} (-1)^{|e(G)|}. \tag{3.12}$$

Here the sum goes over connected subgraphs G whose vertices coincide with the vertices of $G(X)$ and $|e(G)|$ is the number of edges of the graph G. If the cluster X contains only one contour, then $a(X) = 1$.

Note that the number of contours Γ with $|S(\Gamma)| = s$, $L(\Gamma) = n$, whose support contains a given site can be bounded by $2^s \nu_d^n$ where $\nu_2 = 4$ and $\nu_3 = 14^2$.

As a result of standard cluster expansion we get that for $\kappa e^{-\alpha} < 1$, where $\kappa = 2\nu_d \kappa_{\mathrm{cl}}$ and $\kappa_{\mathrm{cl}} \equiv \frac{\sqrt{5}+3}{2} e^{\frac{2}{\sqrt{5}+1}}$ is the cluster constant:[20]

$$\ln \Xi'_q(\Lambda; \mu_1, \mu_2) = g_q|\Lambda| + \sum_{X:\mathrm{supp}X \subset \Lambda} \Phi_q(X) \tag{3.13}$$

$$= g_q|\Lambda| + |\Lambda| \sum_{X:\mathrm{supp}X \ni x} \frac{\Phi_q(X)}{|\mathrm{supp}\ X|} + \sigma(\Lambda \mid \Phi_q), \tag{3.14}$$

where

$$\sigma(\Lambda \mid \Phi_q) = - \sum_{X:\mathrm{supp}X \cap \Lambda^c \neq \emptyset} \frac{|\mathrm{supp}X \cap \Lambda|}{|\mathrm{supp}\ X|} \Phi_q(X). \tag{3.15}$$

In addition (see Section 6):

$$\sum_{X:\mathrm{supp}X \ni x} \left|\Phi_q(X)\right| \leqslant \kappa e^{-\alpha}, \tag{3.16}$$

$$\left|\sigma(\Lambda \mid \Phi_q)\right| \leqslant \kappa e^{-\alpha}\, |\partial \Lambda|, \tag{3.17}$$

giving

$$p_q(\mu_1, \mu_2) = g_q + \sum_{X:\mathrm{supp}\ X \ni x} \frac{\Phi_q(X)}{|\mathrm{supp}\ X|}. \tag{3.18}$$

The following theorem shows that the low temperature phase diagram of the model is a small perturbation of the diagram of ground states (see Fig. 3).

Theorem 2. Assume β is large enough so that $e^{-\beta J+5} = e^{-\alpha} < \frac{1}{2(d+1)\kappa}$, then there exists a coexistence line $\ln(e^{\mu_1^*} + e^{\mu_2^*}) = O(e^{-2d\beta J})$ on which all mixt-contours and all emp-contours are stable and such that:

$$\Xi_q(\Lambda; \mu_1^*, \mu_2^*) = \Xi'_q(\Lambda; \mu_1^*, \mu_2^*). \tag{3.19}$$

for both boundary conditions $q = \mathrm{mixt}$ and $q = \mathrm{emp}$, and the pressure is given by

$$p(\mu_1^*, \mu_2^*) = p_{\mathrm{mixt}}(\mu_1^*, \mu_2^*) = p_{\mathrm{emp}}(\mu_1^*, \mu_2^*). \tag{3.20}$$

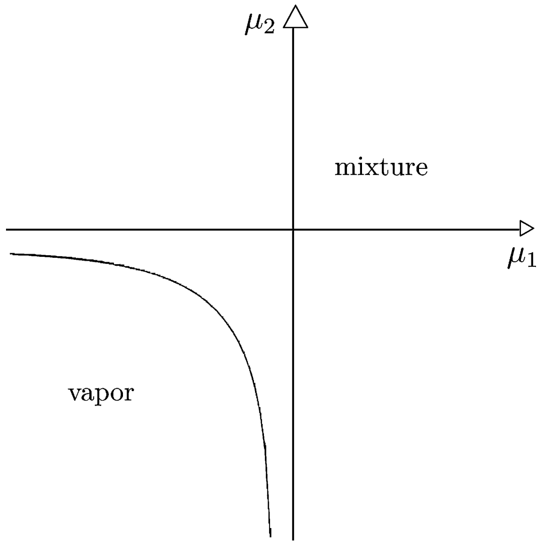

Fig. 3. Phase diagram at low temperature.

For any $t > 0$

$$\Xi_{\text{mixt}}(\Lambda; \mu_1^* + t, \mu_2^* + t) = \Xi'_{\text{mixt}}(\Lambda; \mu_1^* + t, \mu_2^* + t), \tag{3.21}$$

$$p(\mu_1^* + t, \mu_2^* + t) = p_{\text{mixt}}(\mu_1^* + t, \mu_2^* + t) > p_{\text{emp}}(\mu_1^* + t, \mu_2^* + t)$$

and

$$\Xi_{\text{emp}}(\Lambda; \mu_1^* - t, \mu_2^* - t) = \Xi'_{\text{emp}}(\Lambda, ; \mu_1^* - t, \mu_2^* - t), \tag{3.22}$$

$$p(\mu_1^* - t, \mu_2^* - t) = p_{\text{emp}}(\mu_1^* - t, \mu_2^* - t) > p_{\text{mixt}}(\mu_1^* - t, \mu_2^* - t).$$

The proof is postponed to Section 6.

Whenever a cluster X contains only one contour Γ ($X(\Gamma) = 1$ and $X(\Gamma') = 0$ for $\Gamma' \neq \Gamma$) one has $\Phi_q(X) = z_q(\Gamma)$. From this property we get that the metastable pressures read:

$$p_{\text{mixt}}(\mu_1, \mu_2) = \ln(e^{\mu_1} + e^{\mu_2}) + \frac{(e^{\mu_1 - \beta J_1} + e^{\mu_2 - \beta J_2})^{2d}}{(e^{\mu_1} + e^{\mu_2})^{2d+1}} + O\big(e^{-(2d+1)\beta J}\big), \tag{3.23}$$

$$p_{\text{emp}}(\mu_1, \mu_2) = e^{\mu_1 - 2d\beta J_1} + e^{\mu_2 - 2d\beta J_2} + O\big(e^{-(2d+1)\beta J}\big). \tag{3.24}$$

Equalizing (3.23) with (3.24) gives the first term of the equation for the coexistence line stated in Theorem 2.

Let us introduce the infinite volume expectation $\langle\cdot\rangle^{\text{bc}}(\mu_1,\mu_2)$ associated to the Gibbs measure (2.16):

$$\langle\cdot\rangle^{\text{bc}}(\mu_1,\mu_2)=\lim_{\Lambda\uparrow\mathbb{Z}^d}\sum_{\mathbf{s}_\Lambda\in\Omega^\Lambda}\cdot\,\mathbb{P}_\Lambda^{\text{bc}}(\mathbf{s}_\Lambda). \tag{3.25}$$

As a consequence of the cluster expansion we have for any $t\geqslant 0$:

$$\begin{aligned}\langle\delta(s_x,1)+\delta(s_x,2)\rangle^{\text{mixt}}(\mu_1^*+t,\mu_2^*+t) &= \langle 1-\delta(s_x,0)\rangle^{\text{mixt}}(\mu_1^*+t,\mu_2^*+t)\\ &\geqslant 1-O\big(e^{-2d\beta J}\big), &(3.26)\\ \langle\delta(s_x,1)+\delta(s_x,2)\rangle^{\text{emp}}(\mu_1^*-t,\mu_2^*-t) &= \langle 1-\delta(s_x,0)\rangle^{\text{emp}}(\mu_1^*-t,\mu_2^*-t)\\ &\leqslant O\big(e^{-2d\beta J}\big), &(3.27)\end{aligned}$$

This shows that the model exhibits at low temperature a first-order phase transition at the coexistence line where the pressure is discontinuous.

Let, $c_i=\frac{\partial p_{\text{mixt}}(\mu_1,\mu_2)}{\partial\mu_i}|_{\mu_1=\mu_1^*,\mu_2=\mu_2^*}$, $i=1,\,2$ be the density of the particle i in the mixture regime, on the coexistence line, and let

$$\begin{aligned}d_i &= \frac{\partial}{\partial\mu_i}\sum_{X:\text{supp }X\ni x}\frac{\Phi_{\text{mixt}}(X)}{|\text{supp }X|}\Bigg|_{\mu_1=\mu_1^*,\mu_2=\mu_2^*}\\ &= 2de^{\mu_i^*-\beta J_i}\frac{(e^{\mu_1^*-\beta J_1}+e^{\mu_2^*-\beta J_2})^{2d-1}}{(e^{\mu_1^*}+e^{\mu_2^*})^{2d+1}}\\ &\quad -(2d+1)e^{\mu_i^*}\frac{(e^{\mu_1^*-\beta J_1}+e^{\mu_2^*-\beta J_2})^{2d}}{(e^{\mu_1^*}+e^{\mu_2^*})^{2d+2}}+O\big(e^{-(2d+1)\beta J}\big)\end{aligned}$$

for $i=1,\,2$. One has

$$\begin{aligned}c_i &= \frac{e^{\mu_i^*}}{e^{\mu_1^*}+e^{\mu_2^*}}+d_i=\frac{e^{\mu_i^*}}{e^{\mu_1^*}+e^{\mu_2^*}}(1+(e^{\mu_1^*}+e^{\mu_2^*})d_i)\\ &= \frac{e^{\mu_i^*}}{e^{\mu_1^*}+e^{\mu_2^*}}\big(1+O\big(e^{-2d\beta J}\big)\big). &(3.28)\end{aligned}$$

4. SURFACE TENSIONS

To introduce the surface tension between the mixture and the vapor, we consider the parallelepipedic box:

$$V = V_{L,M} = \Big\{(x_1, .., x_d) \in \mathbb{Z}^d : |x_i| \leqslant L, i = 1, ..., d-1; -M \leqslant x_d \leqslant M-1\Big\}.$$

Let $\partial_+ V$ (respectively, $\partial_- V$) be the set of sites of ∂V with $x_d \geqslant 0$ (respectively, $x_d < 0$). We introduce the boundary condition

$$\chi^{\text{mixt,emp}}(\mathbf{s}_V) = \prod_{x \in \partial_- V} (1 - \delta(s_x, 0)) \prod_{x \in \partial_+ V} \delta(s_x, 0).$$

This boundary condition enforces the existence of an interface (see below for its precise definition) between the mixture and the vapor. The interfacial tension between the mixture and the vapor is defined by the limit

$$\tau_{\text{mixt,emp}} = \lim_{L \to \infty} \lim_{M \to \infty} \frac{F(V)}{(2L+1)^{d-1}}, \tag{4.1}$$

where

$$F(V) = -\frac{1}{\beta} \ln \frac{\Xi_{\text{mixt,emp}}(V; \mu_1^*, \mu_2^*)}{(\Xi_{\text{mixt}}(V; \mu_1^*, \mu_2^*)\, \Xi_{\text{emp}}(V; \mu_1^*, \mu_2^*))^{1/2}}. \tag{4.2}$$

This definition is justified by noticing that in this expression the volume terms proportional to the free energy of the coexisting phases, as well as the terms corresponding to the boundary effects, cancel and only the term that takes into account the free energy of the interface is left.

To give a precise description of interfaces, we let $\mathbb{L}_+$ denotes the semi-infinite lattice with $x_d \geqslant 0$ and let $\mathbb{L}_- = \mathbb{Z}^d \setminus \mathbb{L}_+$ denotes its complement. Consider then a configuration $\mathbf{s} \in \Omega^{\mathbb{Z}^d}$, with empty sites on $\partial_+ V$ and on $\mathbb{L}_+ \setminus V$ and with occupied sites on a $\partial_- V$ and on $\mathbb{L}_- \setminus V$. The boundary $B(\mathbf{s})$ (set of pairs $\{s_x, s_y\}$ such that $s_x \neq 0$ and $s_y = 0$) of such configuration necessarily contains an infinite component I_∞ whose support outside the box V is the set of n.n. pairs between $\mathbb{L}_+$ and $\mathbb{L}_-$.

We call interface I the part of I_∞ whose support lies inside the box V: $I_\infty \setminus I$, is called extension of I (see Fig. 4). As it was done for contours, we use $S_\alpha(I)$ to denote the set of sites for which $s_x = \alpha$. The set $\operatorname{supp} I = S_0(I) \cup S_1(I) \cup S_2(I)$ is called support of the interface I. We will also use $S(I) = S_1(I) \cup S_2(I)$ to denote the set of occupied sites of the interface,

0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	1	2	0	0	0	0
0	**0**	**0**	**0**	**0**	**0**	0	0	1	2	1	0	0	0
0	**2**	**1**	**1**	**1**	**2**	**0**	0	0	0	0	0	0	0
0	**0**	**0**	**1**	2	**2**	**0**	**0**	**0**	**0**	**0**	**0**	0	0
0	**0**	**0**	**1**	2	**2**	**0**	**1**	**2**	**1**	**2**	**1**	**0**	**0**
1	**2**	**1**	2	2	**1**	**0**	**2**	2	2	2	1	**2**	**1**
2	2	1	1	2	**1**	**0**	**2**	2	2	1	1	1	1
2	1	1	2	1	1	**1**	1	0	0	2	2	1	2
1	2	0	1	1	2	1	2	0	0	2	1	1	1
2	1	1	1	1	2	2	1	2	2	2	2	2	1
2	1	2	2	2	1	2	1	2	1	1	1	2	2

Fig. 4. Interface of a configuration with the mixt, emp boundary condition.

$L_1(I)$ (respectively, $L_2(I)$) to denote the number of nearest–neighbor pairs $\langle x, y\rangle$ such that $s_x = 1$ and $s_y = 0$ (respectively, $s_x = 2$ and $s_y = 0$) and $L(I) = L_1(I) + L_2(I)$.

The set $V \setminus S(I)$ splits into a part D below the interface and a part U above the interface: if one consider the configuration whose boundary contains only the interface I, D is the subset of $V \setminus S(I)$ with occupied sites and U is the subset of $V \setminus S(I)$ with empty sites.

Then, the partition function, with mixed boundary conditions, can be expanded over interfaces as follows

$$\Xi_{\text{mixt,emp}}(V; \mu_1^*, \mu_2^*) = \sum_{I:\text{supp } I \subset V} \omega(I)\, \Xi_{\text{mixt}}(D; \mu_1^*, \mu_2^*)\, \Xi_{\text{emp}}(U; \mu_1^*, \mu_2^*), \tag{4.3}$$

where

$$\omega(I) = e^{-\beta J_1 L_1(I) - \beta J_2 L_2(I) + \mu_1^* |S_1(I)| + \mu_2^* |S_2(I)|}. \tag{4.4}$$

Therefore,

$$e^{-\beta F(V)} = \sum_{I:\text{supp } I \subset V} \omega(I) \frac{\Xi_{\text{mixt}}(D; \mu_1^*, \mu_2^*)\, \Xi_{\text{emp}}(U; \mu_1^*, \mu_2^*)}{(\Xi_{\text{mixt}}(V; \mu_1^*, \mu_2^*)\, \Xi_{\text{emp}}(V; \mu_1^*, \mu_2^*))^{1/2}}. \tag{4.5}$$

Since $\Xi_q(\Lambda;\mu_1^*,\mu_2^*)=\Xi'_q(\Lambda;\mu_1^*,\mu_2^*)$ for both empty and mixt boundary conditions, we get by (3.14) and (3.18)

$$\Xi_p(\Lambda;\mu_1^*,\mu_2^*)=\exp\left\{p_q|\Lambda|+\sigma(\Lambda\mid\Phi_q)\right\}.$$

Applying this formula to the various partition functions of (4.5), and taking into account equations (3.20), we get:

$$\begin{aligned}e^{-\beta F(V)} &= \sum_{I:\mathrm{supp}\ I\subset V}\omega(I)e^{-p(\mu_1^*,\mu_2^*)|S(I)|+\sigma(D|\Phi_{\mathrm{mixt}})}\\ &\quad +e^{+\sigma(U|\Phi_{\mathrm{emp}})-\frac{1}{2}\sigma(V|\Phi_{\mathrm{mixt}})-\frac{1}{2}\sigma(V|\Phi_{\mathrm{emp}})}.\end{aligned}\tag{4.6}$$

Let $V_+^c=(\mathbb{Z}^d\setminus V)\cap\mathbb{L}_+$ and $V_-^c=(\mathbb{Z}^d\setminus V)\cap\mathbb{L}_-$. We then apply the formula (3.15) to the four last terms of the exponent of the RHS of (4.6) and rewrite the different contributions according to appropriated and natural decompositions of the sets over which the sums take place and collecting analogous terms. Before applying this formula it is convenient first to sum over the clusters with same support. Thus we let

$$\begin{aligned}\tilde\Phi_{\mathrm{mixt}}(C) &= \sum_{X:\mathrm{supp}\ X=C}\Phi_{\mathrm{mixt}}(X),\\ \tilde\Phi_{\mathrm{emp}}(C) &= \sum_{X:\mathrm{supp}\ X=C}\Phi_{\mathrm{emp}}(X).\end{aligned}$$

We then get

$$e^{-\beta F(V)}=e^{-K_V}\sum_{I:\mathrm{supp}\ I\subset V}\omega(I)e^{-p(\mu_1^*,\mu_2^*)|S(I)|}A(I)B_V(I),\tag{4.7}$$

where

$$K_V=\frac{1}{2}\sum_{\substack{C:C\cap V_+^c\neq\emptyset\\ C\cap V_-^c\neq\emptyset}}\tilde\Phi_{\mathrm{mixt}}(C)\frac{|C\cap V|}{|C|}+\frac{1}{2}\sum_{\substack{C:C\cap V_+^c\neq\emptyset\\ C\cap V_-^c\neq\emptyset}}\tilde\Phi_{\mathrm{emp}}(C)\frac{|C\cap V|}{|C|},\tag{4.8}$$

$$A(I)=\prod_{C:C\cap S(I)\neq\emptyset}e^{-\tilde\Phi_{\mathrm{mixt}}(C)\frac{|C\cap D|}{|C|}}\prod_{C:C\cap S(I)\neq\emptyset}e^{-\tilde\Phi_{\mathrm{emp}}(C)\frac{|C\cap U|}{|C|}}\tag{4.9}$$

and

$$B_V(I) = \prod_{\substack{C:C\cap S(I)\neq\emptyset \\ C\cap V_-^c\neq\emptyset}} e^{\tilde{\Phi}_{\text{mixt}}(C)\frac{|C\cap D|}{|C|}} \prod_{C:C\cap V_-^c\neq\emptyset} e^{\tilde{\Phi}_{\text{mixt}}(C)\frac{|C\cap(V\setminus D)|}{|C|}}$$
$$\prod_{\substack{C:C\cap S(I)\neq\emptyset \\ C\cap V_+^c\neq\emptyset}} e^{\tilde{\Phi}_{\text{emp}}(C)\frac{|C\cap U|}{|C|}} \prod_{C:C\cap V_+^c\neq\emptyset} e^{\tilde{\Phi}_{\text{emp}}(C)\frac{|C\cap(V\setminus U)|}{|C|}}. \tag{4.10}$$

In these formula, it is understood that the arguments C of $\tilde{\Phi}_{\text{mixt}}$ and $\tilde{\Phi}_{\text{emp}}$ are, respectively, supports of clusters of mixt-contours and clusters of emp-contours. These functionals satisfy the bound:

$$|\tilde{\Phi}(C)| \leqslant L(C)(\kappa e^{-\alpha})^{L(C)}, \tag{4.11}$$

where $L(C)$ is the number of n.n. pairs of C (see Section 6).

This property allows us to prove that the limit of $F(V)$ when $M\to\infty$ exists, and that, if we denote by $\overline{V}$ the infinite cylinder $\lim_{M\to\infty} V_{L,M}$, then one gets actually $\lim_{M\to\infty} F(V)$ $= F(\overline{V})$ with $F(\overline{V})$ defined as in (4.7)–(4.10). The surface tension then reads

$$\tau_{\text{mixt,emp}} = \lim_{L\to\infty} \frac{F(\overline{V})}{(2L+1)^{d-1}}. \tag{4.12}$$

Clearly the term $K_{\overline{V}}/\beta(2L+1)^{d-1}$ tends to 0 in the limit $L\to\infty$. Let us introduce the modified free energy

$$e^{-\beta F'(\overline{V})} = \sum_{I:\text{supp } I\subset\overline{V}} \omega(I) e^{-p(\mu_1^*,\mu_2^*)|S(I)|} A(I). \tag{4.13}$$

As a consequence of the analysis of Section 7 we shall see that the free energy $F'(\overline{V})$ differs from $F(\overline{V})$ only by a term proportional to L^{d-2}, thus showing that the surface tension is also given by (4.12) with $F(\overline{V})$ replaced by $F'(\overline{V})$. To simplify notations, we shall only consider this last free energy.

In the Solid-On-Solid (SOS) approximation, that we will also consider, the surface tension reads

$$\tau^{\text{SOS}}_{\text{mixt,emp}} = \lim_{L\to\infty} \frac{F^{\text{SOS}}(\overline{V})}{(2L+1)^{d-1}}, \tag{4.14}$$

where

$$F^{\mathrm{SOS}}(\overline{V}) = -\frac{1}{\beta}\ln \sum_{I^{\mathrm{SOS}}:\mathrm{supp}\ I\subset\overline{V}} \omega(I)(e^{\mu_1^*}+e^{\mu_2^*})^{-|S(I)|},$$

where the SOS interfaces belonging to I^{SOS} have no overhangs. This means that the set of dual bonds (in two–dimensions) or dual plaquettes (in three–dimensions) of such interface corresponds to the graph of a function. This approximation may be obtained by adding to the Hamiltonian (2.3) the anisotropic interaction

$$\sum_{\langle x,y\rangle}^{\mathrm{vert}} J'\left[\delta(s_x,0)(1-\delta(s_y,0))+(1-\delta(s_x,0))\delta(s_y,0)\right],$$

where the sum $\sum^{\mathrm{vert}}$ is over vertical bonds, and then taking, with an appropriated normalization, the limit $J'\to\infty$. The coexistence line in that approximation coincides with the ground states coexistence line, $e^{\mu_1^*}+e^{\mu_2^*}=1$, so that:

$$e^{-\beta F^{\mathrm{SOS}}(\overline{V})} = \sum_{I^{\mathrm{SOS}}:\mathrm{supp}\ I\subset\overline{V}} \omega(I). \tag{4.15}$$

Let us now define the surface tensions between each species of the mixture and the vapor. As mentioned in the introduction, whenever either the particles 1 or the particles 2 are not allowed the system reduces to the usual Ising model in its lattice gas version. Thus, we introduce the configurations $n_V\in\{0,1\}^V$ of the lattice gas and the following partition functions

$$Q_\alpha(V) = \sum_{n_V\in\{0,1\}^V} \exp\left\{\beta J_\alpha \sum_{\langle x,y\rangle\subset V}[n_x(1-n_y)+(1-n_x)n_y]\right\}\prod_{x\in\partial V} n_x,$$

$$Q_{\alpha,0}(V) = \sum_{n_V\in\{0,1\}^V} \exp\left\{\beta J_\alpha \sum_{\langle x,y\rangle\subset V}[n_x(1-n_y)+(1-n_x)n_y]\right\} \times \prod_{x\in\partial_- V}(1-n_x)\prod_{x\in\partial_+ V} n_x$$

for $\alpha=1$ and $\alpha=2$.

The interfacial tension between the species $\alpha = 1, 2$, and the vapor is the limit[18,21]

$$\tau_{\alpha,0} = \lim_{L\to\infty} \lim_{M\to\infty} \frac{F_\alpha(V)}{(2L+1)^{d-1}},$$

where

$$F_\alpha(V) = -\frac{1}{\beta} \ln \frac{Q_{\alpha,0}(V)}{Q_\alpha(V)}.$$

It is well known that the ratio $Q_{\alpha,0}(V)/Q_\alpha(V)$ can be expressed as a sum over interfaces which in this case are connected set of bonds or plaquettes of the dual lattice[11,12]. Extracting the energy of the flat interface, the system can be written as a gas of excitations leading to

$$F_\alpha(V) = J_\alpha(2L+1)^{d-1} + F_\alpha^{\mathrm{ex}}(V).$$

In two-dimensions, F_α^{ex} is the free energy of the gas of jumps of the Gallavotti's line.[11] In three-dimensions, F_α^{ex} is the free energy of the gas of walls of the Dobrushin's interface.[12] In both cases these free energies can be analyzed by cluster expansion techniques at low temperatures. Namely, the specific free energies $\mathcal{F}_\alpha = \lim_{L\to\infty} F_\alpha^{\mathrm{ext}}(V)/(2L+1)^{d-1}$ exist and are given by convergent expansions in term of the activities $e^{-\beta J_\alpha}$, giving

$$\beta\tau_{\alpha,0} = \beta J_\alpha + \beta\mathcal{F}_\alpha. \tag{4.16}$$

In addition

$$-\beta\mathcal{F}_\alpha = 2e^{-\beta J_\alpha} + O(e^{-2\beta J_\alpha}) \quad \text{for} \quad d=2, \tag{4.17}$$
$$-\beta\mathcal{F}_\alpha = 2e^{-4\beta J_\alpha} + O(e^{-6\beta J_\alpha}) \quad \text{for} \quad d=3. \tag{4.18}$$

We refer the reader also to refs. 22–24 and references therein for the study of these expansions. Furthermore, in two-dimensions the surface tension defined above is known to coincide with the one computed by Onsager.[18] We thus have an exact expression for $\tau_{\alpha,0}$, and for $\mathcal{F}_\alpha$:

$$\beta\mathcal{F}_\alpha = \ln\tanh(\beta J_\alpha/2) \tag{4.19}$$

for βJ_α larger than the critical value $\ln(1+\sqrt{2})$.

Similar results hold in the corresponding SOS approximation (see ref. 25 for the three-dimensional case). We will use $\tau^{\text{SOS}}_{\alpha,\text{emp}}$ and $\mathcal{F}^{\text{SOS}}_{\alpha}$ the surface tensions and free energies in this approximation. In two-dimensions $\mathcal{F}^{\text{SOS}}_{\alpha}$ is also exactly known[26] and also given by (4.19), but for all temperatures:

$$\beta\mathcal{F}^{\text{SOS}}_{\alpha} = \ln\tanh(\beta J_\alpha/2) \tag{4.20}$$

for $\beta \geqslant 0$.

5. MAIN RESULTS

In this section we will give a relationship between the surface tensions introduced in the previous section.

The leading term of the free energy $F'(\overline{V})$ corresponds to flat interfaces without any decoration. They are those interfaces, for which the set of n.n. x, y such that x is empty and y is occupied crosses the plane $x_d = -1/2$, and such that $A(I) = 1$. Let $\mathcal{I}_{\text{flat}}$ be the set of flat interfaces and $N = (2L+1)^{d-1}$. We have

$$\begin{aligned}
e^{-\beta F_{\text{flat}}(\overline{V})} &\equiv \sum_{\substack{I:\text{supp } I\subset\overline{V} \\ I\in\mathcal{I}_{\text{flat}}}} \omega(I) e^{-p(\mu_1^*,\mu_2^*)|S(I)|} \\
&= \sum_{n=0}^{N} \binom{N}{n} e^{(\mu_1^*-\beta J_1)n} e^{(\mu_1^*-\beta J_2)(N-n)} e^{-p(\mu_1^*,\mu_2^*)N} \\
&= (c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2})^N,
\end{aligned}$$

where

$$c_1^* = e^{\mu_1^* - p(\mu_1^*,\mu_2^*)}, \quad c_2^* = e^{\mu_2^* - p(\mu_1^*,\mu_2^*)}. \tag{5.1}$$

We will show in Section 7 that the difference $F'(\overline{V}) - F_{\text{flat}}(\overline{V})$ can be expressed as a free energy of a gas of excitations called aggregates. It will then turns out that the limit

$$\mathcal{F} = \lim_{L\to\infty} \frac{F'(\overline{V}) - F_{\text{flat}}(\overline{V})}{N}, \tag{5.2}$$

exists and is given by a convergent expansion at low temperatures, see (7.17).

Theorem 3. Assume β is large enough so that $8e(e-1)\kappa^2 e^{-\beta J+5} < 1$, then the interfacial tensions $\tau_{\text{mixt,emp}}$, $\tau_{1,0}$ and $\tau_{2,0}$ satisfy the equation:

$$e^{-\beta(\tau_{\text{mixt,emp}}-\mathcal{F})} = c_1^* e^{-\beta(\tau_{1,0}-\mathcal{F}_1)} + c_2^* e^{-\beta(\tau_{2,0}-\mathcal{F}_2)}, \tag{5.3}$$

where

$$c_i^* = e^{\mu_i^* - p(\mu_1^*,\mu_2^*)}, \tag{5.4}$$

$\mathcal{F}$ is the convergent series defined by (7.17):

$$-\beta\mathcal{F} = \frac{c_1^* e^{-5\beta J_1} + c_2^* e^{-5\beta J_2}}{c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2}} + \frac{(c_1^* e^{-2\beta J_1} + c_2^* e^{-2\beta J_2})^4}{(c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2})^4} + O(e^{-5\beta J}) \tag{5.5}$$

in dimension $d=3$ and

$$-\beta\mathcal{F} = 2\frac{c_1^* e^{-2\beta J_1} + c_2^* e^{-2\beta J_2}}{c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2}} + O(e^{-2\beta J}) \tag{5.6}$$

in dimension $d=2$, and the convergent series $\mathcal{F}_\alpha$ satisfies (4.17)–(4.19).

The proof is postponed to Section 7.

Some remarks and comments are in order.

The densities c_i are easily related to the c_i^* through the relation (see (3.23) and (3.28)):

$$c_i^* = c_i \frac{(e^{\mu_1^*} + e^{\mu_2^*}) e^{-p_{\text{mixt}}(\mu_1^*,\mu_2^*)}}{1 + (e^{\mu_1^*} + e^{\mu_2^*}) d_i} \tag{5.7}$$

$$= c_i \Big[1 - \big(c_1 e^{-\beta J_1} + c_2 e^{-\beta J_2}\big)^{2d} - 2d c_i e^{-\beta J_i} \big(c_1 e^{-\beta J_1} + c_2 e^{-\beta J_2}\big)^{2d-1}$$
$$- 2(d+1) c_i \big(c_1 e^{-\beta J_1} + c_2 e^{-\beta J_2}\big)^{2d} + O\big(e^{-(2d+1)\beta J}\big) \Big]. \tag{5.8}$$

In the SOS approximation, as mentioned in Section 4, the coexistence line is given by $e^{\mu_1^*} + e^{\mu_1^*} = 1$ and the densities of each species in the mixture regime on this line are $c_1 = e^{\mu_1^*}$ and $c_2 = e^{\mu_2^*}$. We have

$$e^{-\beta F_{\text{flat}}^{\text{SOS}}(\overline{V})} \equiv \sum_{\substack{I:\text{supp } I \subset \overline{V} \\ I \in \mathcal{I}_{\text{flat}}}} \omega(I) = (c_1 e^{-\beta J_1} + c_2 e^{-\beta J_2})^N$$

and the equation between the surface tensions reads

$$e^{-\beta(\tau^{\rm SOS}_{\rm mixt,emp}-\mathcal{F}^{\rm SOS})}=c_1e^{-\beta(\tau^{\rm SOS}_{1,0}-\mathcal{F}^{\rm SOS}_1)}+c_2e^{-\beta(\tau^{\rm SOS}_{2,0}-\mathcal{F}^{\rm SOS}_2)}. \tag{5.9}$$

Here $\mathcal{F}^{\rm SOS}=\lim_{L\to\infty}\frac{F^{\rm SOS}(\overline{V})-F^{\rm SOS}_{\rm flat}(\overline{V})}{N}$: it can be expressed as the series given by (7.17), but with truncated functional corresponding to the activities

$$z^{\rm SOS}(W)=e^{-\beta J_1L_1(W)-\beta J_2L_2(W)+\mu_1^*|S_1(W)|+\mu_2^*|S_2(W)|}$$

and satisfy also relations (5.5) and (5.6) with c_i^* replaced by c_i.

To find an exact solution for $\mathcal{F}^{SOS}$ in two-dimensions seems to be an interesting problem. Actually, this would give an exact equation for the surface tensions not restricted to low temperatures.[27]

The method developed here can be extended naturally to finite range interactions. As an example, we can consider the Hamiltonian (2.3) with the sum over nearest-neighbors and next nearest-neighbors. In that case we found that the corresponding surface tensions satisfy, in two-dimensions and at low enough temperatures, the equation

$$\begin{aligned}e^{-\beta(\tau_{\rm mixt,emp}-\mathcal{F})}&=c_1^*e^{-3\beta J_1}+c_2^*e^{-3\beta J_2}\\&=c_1^*e^{-\beta(\tau_{1,0}-\mathcal{F}_1)}+c_2^*e^{-\beta(\tau_{2,0}-\mathcal{F}_2)},\end{aligned}$$

where

$$-\beta\mathcal{F}_1=2e^{-\beta J_1}+O(e^{-2\beta J_1}),\quad -\beta\mathcal{F}_2=2e^{-\beta J_2}+O(e^{-2\beta J_2})$$

and

$$\begin{aligned}-\beta\mathcal{F}=&\frac{c_1^{*3}e^{-7\beta J_1}+c_1^{*2}c_2^*(e^{-6\beta J_1-J_2}+e^{-5J_1-2J_2}+e^{-4J_1-3J_2})}{(c_1^*e^{-3\beta J_1}+c_2^*e^{-3\beta J_1})^2}\\&+\frac{c_1^*c_2^{*2}(e^{-3\beta J_1-4J_2}+e^{-2J_1-5J_2}+e^{-J_1-7J_2})+c_2^{*3}e^{-7\beta J_2}}{(c_1^*e^{-3\beta J_1}+c_2^*e^{-3\beta J_1})^2}+O(e^{-2\beta J})\end{aligned}$$

with $c_i^*=c_i\big(1+O(e^{-8\beta J})\big)$.

When the hypothesis (2.2) or (2.7) on the model defined by Hamiltonian (2.1) or (2.5) is not satisfied, with $\mathcal{J}>0$, there are, at low temperatures, two phases rich in particles of species 1 or of species 2 as been proved in ref. 10 for $\mathcal{C}=0$. This can be also shown for $\mathcal{C}\neq 0$ provided that the three quantities in equations (2.6) are positive. Indeed the Hamiltonian (2.1) and (2.5) can be reduced, up to chemical potential terms, to the form

$$H = \sum_{\langle x,y\rangle} \Big[J_1\big(\delta(s_x,1)\delta(s_y,0)+\delta(s_x,0)\delta(s_y,1)\big) \\ +J_2\big(\delta(s_x,2)\delta(s_y,0)+\delta(s_x,0)\delta(s_y,2)\big) \\ +\frac{\mathcal{J}}{4}\big(\delta(s_x,1)\delta(s_y,2)+\delta(s_x,2)\delta(s_y,1)\big)\Big], \tag{5.10}$$

where $J_1 = 2\mathcal{J}+\mathcal{K}+2\mathcal{C}$, $J_1 = 2\mathcal{J}+\mathcal{K}-2\mathcal{C}$, and $\mathcal{J}$ are positive constants. In this situation and with fixed concentration of the species either we are in one of these two pure phases that coexist with the gaseous phase or in the coexistence of the three phases. In the later case, there will be segregation between the three phases and one will observe only the three kinds of interfaces between these phases. One cannot truly speak in this approach about a real surface tension of a mixture.

Let us stress that from our Eqs. (5.3) and (5.9), we get obviously the Guggeinheim relation (1.1) by neglecting the terms exponentially small with the inverse temperature, i.e. $\mathcal{F}, \mathcal{F}_1$ and $\mathcal{F}_2$. This shows that this relation provides a good approximation at very low temperatures.

To see the quantitative difference between the above equations, let us consider a concrete example. Note that when we take only into account the (exponentially) smallest order corrections in our equations, they reads (in dimension 3):

$$\tau_{\text{mixt,emp}} = -\frac{kT}{a^2}\ln\left[c_1 e^{-\frac{a^2\tau_{1,0}}{kT}-2e^{-\frac{4a^2\tau_{1,0}}{kT}}} + (1-c_1)e^{-\frac{a^2\tau_{2,0}}{kT}-2e^{-\frac{4a^2\tau_{2,0}}{kT}}}\right] \\ +kT\frac{c_1e^{-(5a^2\tau_{1,0})/(kT)}+(1-c_1)e^{-(5a^2\tau_{2,0})/(kT)}}{c_1e^{-(a^2\tau_{1,0})/(kT)}+(1-c_1)e^{-(a^2\tau_{2,0})/(kT)}} \\ +kT\left[\frac{c_1e^{-(2a^2\tau_{1,0})/(kT)}+(1-c_1)e^{-(2a^2\tau_{2,0})/(kT)}}{c_1e^{-(a^2\tau_{1,0})/(kT)}+(1-c_1)e^{-(a^2\tau_{2,0})/(kT)}}\right]^4, \tag{5.11}$$

where a is the lattice spacing and k the Boltzman constant, while for the Guggenheim relation, one has

$$\tau^{\text{Gugg}}_{\text{mixt,emp}} = -\frac{kT}{a^2}\ln\left[c_1e^{-\frac{a^2\tau_{1,0}}{kT}}+(1-c_1)e^{-\frac{a^2\tau_{2,0}}{kT}}\right]. \tag{5.12}$$

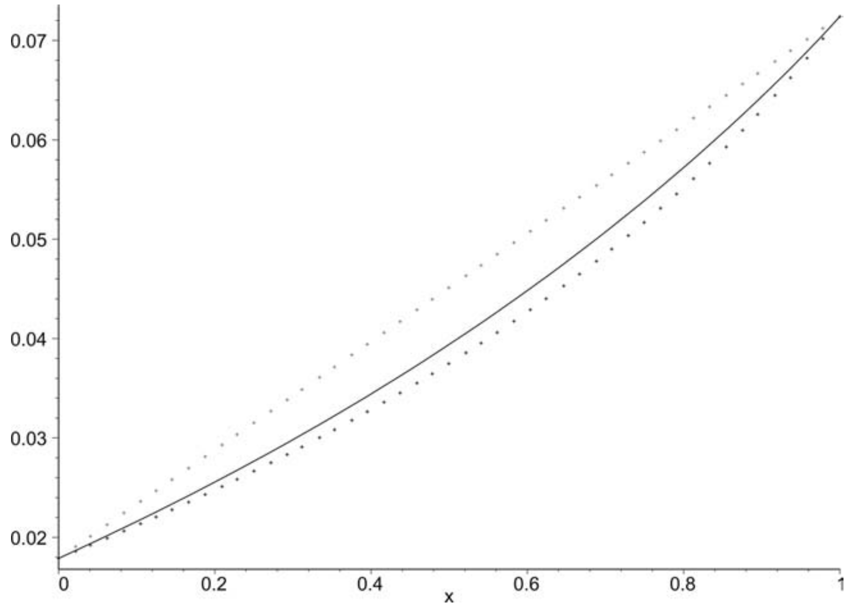

Fig. 5. Plot of the surface tension given by (5.11) (solid curve) as function of the concentration c_1. The dotted curve corresponds to formula (5.12) and the dotted line to formula (5.13).

Note also that the simplest form of Eqs. (1.2) and (1.3) reads

$$\tau_{(1,2)|0} = c_1 \tau_{1,0} + (1 - c_1)\tau_{2,0}. \tag{5.13}$$

Figure 5 shows that there is actually a quantitative difference between the Eqs. (5.11) and (5.12). We have chosen a mixture of water and hexane, i.e. $\tau_{1,0} = 0.0724\,\mathrm{N}\,/\,\mathrm{m}$, $\tau_{2,0} = 0.01978\ \mathrm{N}\,/\,\mathrm{m}$, $a = 3\mathring{\mathrm{A}}$, the size of a water molecule, and the temperature $T = 300\ \mathrm{K}$.

Finally, notice that when the coupling constants J_1 and J_2 (or equivalently the surface tensions $\tau_{1,0}$ and $\tau_{2,0}$) differ appreciably, we get assuming $J_1 < J_2$, and neglecting in Eqs. (5.11) and (5.12) the terms exponentially small with respect to the inverse temperature:

$$\frac{\tau_{\mathrm{mixt,emp}}}{\tau_{1,0}} = 1 - \frac{1}{\beta J_1} \ln(1 - c_2^*) \tag{5.14}$$

to be compared with Szyzkowsky's equation (1.4).

6. PROOF OF THEOREM 2

Let us first give the proof of relations (3.13)–(3.17).

Let $\mu(\Gamma)=(a\nu e^{\lambda})^{-L(\Gamma)}$, with $\nu=2\nu_d$, $a>1$, and $\lambda>0$, then

$$\sum_{\Gamma\nsim\Gamma_0}\mu(\Gamma)\leqslant L(\Gamma_0)\sum_{n=1}^{\infty}e^{-\lambda n}a^{-n}\leqslant\frac{e^{-\lambda}}{a-1}L(\Gamma_0), \tag{6.1}$$

where the sum runs over contours Γ incompatible with a given contour Γ_0.

The condition $\nu e^{-(\alpha-\lambda)}ae^{\frac{1}{a-1}}\leqslant 1$ actually ensures that the convergence condition

$$\left|z'_q(\Gamma_0)\right|\leqslant\left(e^{\mu(\Gamma_0)}-1\right)\exp\left[-\sum_{\Gamma\nsim\Gamma_0}\mu(\Gamma)\right] \tag{6.2}$$

of ref. 19 is fulfilled. We then choose $a=\frac{\sqrt{5}+3}{2}$ (that minimizes $ae^{\frac{1}{a-1}}$) getting by ref. 19 for $\kappa\leqslant e^{(\alpha-\lambda)}$ the equality (3.13) and

$$\sum_{X:X(\Gamma)\geqslant 1}|\Phi_q(X)|\leqslant\mu(\Gamma). \tag{6.3}$$

The invariance of the Φ_q under translations leads to (3.14). On the other hand the last inequality gives

$$\sum_{X:\mathrm{supp}X\ni x}\left|\Phi_q(X)\right|\leqslant\sum_{\Gamma:\mathrm{supp}\ \Gamma\ni x}\ \sum_{X:X(\Gamma)\geqslant 1}\left|\Phi_q(X)\right| \tag{6.4}$$

$$\leqslant\sum_{\Gamma:\mathrm{supp}\ \Gamma\ni x}\mu(\Gamma)\leqslant\frac{e^{-\lambda}}{a_0-1}\leqslant\kappa e^{-\alpha} \tag{6.5}$$

by choosing $e^{-\lambda}=\kappa e^{-\alpha}$ and taking into account that $a_0-1\geqslant 1$; here the first sum is over all multi-indexes X whose support contains a given point x. This implies (3.16) and also (3.17) since $\left|\sigma(\Lambda\mid\Phi_q)\right|\leqslant|\partial\Lambda|\sum_{X:\mathrm{supp}\ X\ni x}\left|\Phi_q(X)\right|$. Note furthermore that one easily gets the bound (4.11) from relations (6.1) and (6.3)

We shall also gives a bound needed below. Define the diameter of a contour Γ as $\mathrm{diam}\,\Gamma=\max_{x,y\in X(\Gamma)}d(x,y)$ where $d(x,y)$ is the distance between the site x and y. Then

$$\sum_{\substack{X:\operatorname{supp} X\ni x\\ \operatorname{diam}\operatorname{supp} X\geqslant A}} \left|\Phi_q(X)\right| \leqslant \sum_{\substack{\Gamma:S(\Gamma)\ni x\\ \operatorname{diam}\ \Gamma\geqslant A}} \mu(\Gamma) \leqslant \sum_{n\geqslant A}^{\infty} e^{-\lambda n} a^{-n} \leqslant \left(\kappa e^{-\alpha}\right)^{A}. \tag{6.6}$$

We now turn to the proof of Theorem 2. We put $h_q = -p_q$ and

$$a_q = h_q - \min_m h_m. \tag{6.7}$$

The boundary condition q is called stable if $a_q = 0$. Our first step is to show that if the boundary condition q is stable then all q-contours are stable implying that $\Xi'_q(\Lambda;\mu_1,\mu_2)$ coincides with $\Xi_q(\Lambda;\mu_1,\mu_2)$.

We notice that when $a_q \leqslant 1$, then the condition

$$\frac{\Xi_m(\mathrm{Int}_m\ \Gamma;\mu_1,\mu_2)}{\Xi_q(\mathrm{Int}_m\ \Gamma;\mu_0,\mu_1)} \leqslant e^{2|\partial \mathrm{Int}_m\ \Gamma|} \tag{6.8}$$

with $m \neq q$ for a q-contour Γ ensures that this contour is stable, provided

$$e^{-\alpha} \equiv e^{-\beta J+5} < \frac{1}{\kappa}.$$

Indeed by (3.16) $g_{\max} - g_q$ is bounded by $a_q + 2\kappa e^{-\alpha}$. Since $|\partial \mathrm{Int}_m\ \Gamma| \leqslant |L(\Gamma)|$ we get taking into account the Peierls estimate (3.7):

$$\begin{aligned} z_q(\Gamma) &= \omega(\Gamma) e^{-g_{\max}|S(\Gamma)|} e^{(g_{\max}-g_q)|S(\Gamma)|} \frac{\Xi_m(\mathrm{Int}_{\mathrm{mixt}}\ \Gamma;\mu_1,\mu_2)}{\Xi_q(\mathrm{Int}_{\mathrm{mixt}}\ \Gamma;\mu_1,\mu_2)} \\ &\leqslant e^{-(\beta J-5)L(\Gamma)}. \end{aligned}$$

For a volume Λ, we use $\operatorname{diam}\Lambda = \max_{x,y\in\Lambda} d(x,y)$ to denote its diameter. The following proposition show that all q–contours are stable whenever $a_q = 0$.

Proposition 1. Assume β is large enough so that $e^{-\beta J+5} = e^{-\alpha} < \frac{1}{(2d+1)\kappa}$, then

(i) if $a_m \operatorname{diam}\Lambda \leqslant 1$, and $a_q = 0$, then

$$\frac{\Xi_m(\Lambda;\mu_1,\mu_2)}{\Xi_q(\Lambda;\mu_1,\mu_2)} \leqslant e^{a_m|\Lambda| + 2\kappa e^{-\alpha}|\partial\Lambda|}; \tag{6.9}$$

(ii) if $a_q = 0$, then

$$\frac{\Xi_m(\Lambda; \mu_1, \mu_2)}{\Xi_q(\Lambda; \mu_1, \mu_2)} \leqslant e^{3\kappa e^{-\alpha}|\partial\Lambda|}; \tag{6.10}$$

(iii) if $a_m \operatorname{diam} \Lambda \leqslant 1$, then

$$\frac{\Xi_{\widetilde{m}}(\Lambda; \mu_1, \mu_2)}{\Xi_m(\Lambda; \mu_1, \mu_2)} \leqslant e^{(1+5\kappa e^{-\alpha})|\partial\Lambda|}. \tag{6.11}$$

The proof is analog to that of Theorem 3.1 in ref. 28 using our previous estimates. We give it below for the reader's convenience.

We first introduce the notion of small and large contours. We say that a m–contour Γ is small if $a_m \operatorname{diam} \Gamma \leqslant 1$; it is large if $a_m \operatorname{diam} \Gamma > 1$. We also define the partition function $\Xi_q^{\text{small}}(\Lambda)$ which is obtained from $\Xi'_q(\Lambda)$ by replacing the sum over stable contours in (3.9) by a sum over small contours. If we sum instead, only over contours which are at the same time small and stable, we denote the resulting partition function $\Xi_q^{\prime\text{small}}(\Lambda)$. Finally we will use the shorthand notation $\Xi_m(\Lambda)$ for $\Xi_m(\Lambda; \mu_1, \mu_2)$.

We will show the three items of the proposition inductively on $\operatorname{diam} \Lambda$.

Thus we assume that (i)–(iii) have already been proved for all volumes with $\operatorname{diam} \Lambda < k$.

Proof of (i) for $\operatorname{diam} \Lambda = k$.

For any contour Γ in Λ, and any $\widetilde{m}$, we have $\operatorname{diam} \operatorname{Int}_{\widetilde{m}} \Gamma \leqslant k - 1$. We can use the inductive assumptions (ii) and (iii) that all q-contours and all m-contours are stable. Therefore

$$\frac{\Xi_q(\Lambda)}{\Xi_m(\Lambda)} = \frac{\Xi'_q(\Lambda)}{\Xi'_m(\Lambda)}. \tag{6.12}$$

Using the convergence of cluster expansion (3.16) and definition (6.7), one immediately gets (i).

Proof of (ii) for $\operatorname{diam}\ \Lambda = k$

To control the ratio $\Xi_m(\Lambda)/\Xi_q(\Lambda)$, we shall rewrite the partition function $\Xi_m(\Lambda)$ using relation (3.1, and 3.2). Consider for a set of compatible m-contours in Λ, the family $\{\Gamma_1, \ldots, \Gamma_n\}_{\text{ext}}^{\text{large}}$ of its mutually external large m-contours. The others contours are small m–contours in $\operatorname{Int} \equiv$

$\Lambda \setminus \cup_i V(\Gamma_i)$ or any m-contour in $\mathrm{Int} \equiv \cup_i \mathrm{Int}\,\Gamma_i$. Therefore

$$\Xi_m(\Lambda) = \sum_{\{\Gamma_1,\ldots,\Gamma_n\}_{\mathrm{ext}}^{\mathrm{large}}} \Xi_m^{\mathrm{small}}(\mathrm{Ext}) \prod_{i=1}^{n} \omega(\Gamma_i)\, \Xi_m(\mathrm{Int}\,\Gamma_i). \tag{6.13}$$

Dividing and multiplying by $\prod_{i=1}^n e^{g_{\max}|S(\Gamma_i)|}\, \Xi_q(\mathrm{Int}\,\Gamma_i) = \Xi_q(\mathrm{Int}) \prod_{i=1}^n e^{g_q|S(\Gamma_i)|}$, we get

$$\frac{\Xi_m(\Lambda)}{\Xi_q(\Lambda)} = \sum_{\{\Gamma_1,\ldots,\Gamma_n\}_{\mathrm{ext}}^{\mathrm{large}}} \frac{\Xi_m^{\mathrm{small}}(\mathrm{Ext})\, \Xi_q(\mathrm{Int})}{\Xi_q(\Lambda)} \times \prod_{i=1}^{n} e^{g_q|S(\Gamma_i)|} \omega(\Gamma_i) e^{-g_{\max} S(\Gamma_i)|} \frac{\Xi_m(\mathrm{Int}\,\Gamma_i)}{\Xi_q(\mathrm{Int}\,\Gamma_i)}. \tag{6.14}$$

Note that all q-contours in Λ and all small m-contours in Λ are stable by the inductive assumptions (i) and (iii), respectively. Therefore the various partition functions in the first factor of the right-hand side of (6.14) are equal to the corresponding truncated partition functions, which can be controlled by convergent cluster expansion. We get by (3.16)

$$\frac{\Xi_m^{\mathrm{small}}(\mathrm{Ext})\, \Xi_q(\mathrm{Int})}{\Xi_q(\Lambda)} \prod_{i=1}^{n} e^{g_q|S(\Gamma_i)|} \leqslant e^{-h_m^{\mathrm{small}}|\mathrm{Ext}|+h_q|\Lambda\setminus\mathrm{Int}|} \prod_{i=1}^{n} e^{g_q|S(\Gamma_i)|} \times e^{\kappa e^{-\alpha}(|\partial\Lambda|+|\partial\mathrm{Int}|+|\partial\mathrm{Ext}|)},$$

where h_m^{small} is the free energy obtained from Ξ_m^{small}. Using the facts that $|h_q + g_q| \leqslant \kappa e^{-\alpha}$, $|S(\Gamma)| \leqslant |L(\Gamma)|$ and bounding $|\partial\mathrm{Int}| + |\partial\mathrm{Ext}|$ by $|\partial\Lambda| + 2d\sum_i L(\Gamma_i)$, we find

$$\frac{\Xi_m^{\mathrm{small}}(\mathrm{Ext})\, \Xi_q(\mathrm{Int})}{\Xi_q(\Lambda)} \prod_{i=1}^{n} e^{g_q|S(\Gamma_i)|} \leqslant e^{-(h_m^{\mathrm{small}}-h_q)|\mathrm{Ext}|} \times e^{\kappa e^{-\alpha}[2|\partial\Lambda|+(1+2d)\sum_i L(\Gamma_i)]}. \tag{6.15}$$

Combining this bound with (6.14), the Peierls estimates (3.7), the inductive assumption (ii), and $\partial \mathrm{Int}\,\Gamma \leqslant 2dL(\Gamma)$, we get:

$$\begin{aligned}\frac{\Xi^m(\Lambda)}{\Xi^q(\Lambda)} &\leqslant e^{2\kappa e^{-\alpha}|\partial\Lambda|} \sum_{\{\Gamma_1,\ldots,\Gamma_n\}_{\mathrm{ext}}^{\mathrm{large}}} e^{-(h_m^{\mathrm{small}}-h_q)|\mathrm{Ext}|} \prod_{i=1}^n e^{-\beta J|L(\Gamma_i)|} e^{[(8d+1)\kappa e^{-\alpha}]L(\Gamma_i)} \\ &\leqslant e^{2\kappa e^{-\alpha}|\partial\Lambda|} \sum_{\{\Gamma_1,\ldots,\Gamma_n\}_{\mathrm{ext}}^{\mathrm{large}}} e^{-(h_m^{\mathrm{small}}-h_q)|\mathrm{Ext}|} \prod_{i=1}^n e^{-(\alpha+1)L(\Gamma_i)}, \end{aligned} \tag{6.16}$$

where for the last inequality we used the hypothesis $(2d+1)\kappa e^{-\alpha} \leqslant 1$ and $\alpha = \beta J - 5$.

At this point we need a technical lemma proved in ref. 17 (see the proof below).

Lemma 1. Consider the partition function

$$\widetilde{\mathcal{Z}}(\Lambda) = \sum_{\{\Gamma_1,\ldots,\Gamma_n\}_{\mathrm{comp}}} \prod_{i=1}^n \widetilde{z}(\Gamma_i) e^{L(\Gamma_i)} \tag{6.17}$$

of a gas of contours with activities

$$\widetilde{z}(\Gamma) e^{|L(\Gamma)|} \leqslant e^{-\widetilde{\alpha}L(\Gamma)} e^{L(\Gamma)}.$$

Let $-\widetilde{s} = -\lim_{\Lambda\uparrow\mathbb{Z}^d} (1/|\Lambda|) \ln \widetilde{\mathcal{Z}}(\Lambda)$ be the corresponding free energy. Then

$$\sum_{\{\Gamma_1,\ldots,\Gamma_n\}_{\mathrm{ext}}} e^{-a|\mathrm{Ext}|} \prod_{i=1}^n \widetilde{K}(\Gamma_i) \leqslant e^{\kappa e^{-\widetilde{\alpha}+1}|\partial\Lambda|}, \tag{6.18}$$

where the sum is over contours in Λ provided

$$a \geqslant \widetilde{s}, \tag{6.19}$$

$$\kappa e^{-\widetilde{\alpha}+1} \leqslant \frac{1}{2d+1}. \tag{6.20}$$

To apply this lemma to (6.16) we put

$$\widetilde{\alpha} = \alpha + 1, \tag{6.21}$$
$$a = h_m^{\text{small}} - h_p = a_m + h_m^{\text{small}} - h_m \tag{6.22}$$

and

$$\widetilde{z}(S) = \begin{cases} e^{-\widetilde{\alpha} L(\Gamma)} & \text{if } \Gamma \text{ is large,} \\ 0 & \text{if } \Gamma \text{ is small,} \end{cases} \tag{6.23}$$

For $\kappa e^{-\widetilde{\alpha}+1} < 1$, the Mayer expansion for $\ln \widetilde{\mathcal{Z}}(\Lambda)$ is convergent. Using the fact that it only contains large contours ($\operatorname{diam} \Gamma \geqslant 1/a_m$ for each contour contributing to $\ln \widetilde{\mathcal{Z}}(\Lambda)$) one has (see (6.6)):

$$\widetilde{s} \leqslant \left(\kappa e^{-\alpha}\right)^{\frac{1}{a_m}} . \tag{6.24}$$

Moreover the difference $h_m^{\text{small}} - h_m$ is the free energy of a gas of large contours with again $\operatorname{diam} \Gamma \geqslant 1/a_m$ and thus again for $\kappa e^{-\widetilde{\alpha}-1} < 1$ shares the same upper bound

$$\left| h_m^{\text{small}} - h_m \right| \leqslant \left(\kappa e^{-\alpha}\right)^{\frac{1}{a_m}} . \tag{6.25}$$

Hence

$$a - \widetilde{s} \geqslant a_m - 2\left(\kappa e^{-\alpha}\right)^{\frac{1}{a_m}} . \tag{6.26}$$

Therefore the assumption $a - \widetilde{s} \geqslant 0$ will be fulfilled if $a_m \geqslant 2\left(\kappa e^{-\alpha}\right)^{\frac{1}{a_m}}$, i.e. if $(a_m/2)^{a_m} \geqslant \kappa e^{-\alpha}$. This is actually true because the function $(a/2)^a$ has a minimum at $a = 2/e$ for which it takes the value $e^{-2/e} \simeq 0.47$ that is greater than the upper bound $1/(2d+1)$ required for $\kappa e^{-\alpha}$.

Applying the lemma (with the value (6.21)) to(6.16) immediately gives (6.10).

Proof of (iii) for diam $\Lambda = k$.

The inequality (6.11) follows immediately from (6.9), (6.10) , and the fact that

$$a_m |\Lambda| \leqslant a_m \operatorname{diam} \Lambda \, |\partial \Lambda| \leqslant |\partial \Lambda| . \tag{6.27}$$

Proof of Lemma 1. For $\kappa e^{-\widetilde{\alpha}+1} < 1$, the partition function $\widetilde{\mathcal{Z}}(\Lambda)$ can be controlled by convergent cluster expansion. In particular for the interior $\mathrm{Int} = \cup_i \mathrm{Int}\,\Gamma_i$ of a set of external contours $\{\Gamma_1, ..., \Gamma_n\}_{\mathrm{ext}}$ we have the estimate

$$\widetilde{\mathcal{Z}}(\mathrm{Int}) e^{-\widetilde{s}|\mathrm{Int}|} \geqslant e^{-\kappa e^{-\widetilde{\alpha}+1}|\partial \mathrm{Int}|} \geqslant \prod_{i=1}^{n} e^{-2d\kappa e^{-\widetilde{\alpha}+1}|L(\Gamma_i)|}. \tag{6.28}$$

Here the first inequality stems from (3.17) and the last from the hypothesis (6.20). Therefore

$$\begin{aligned}\sum_{\{\Gamma_1,...,\Gamma_n\}_{\mathrm{ext}}} e^{-a|Ext|} \prod_{i=1}^{n} \widetilde{z}(\Gamma_i) &\leqslant \sum_{\{\Gamma_1,...,\Gamma_n\}_{\mathrm{ext}}} e^{-a|\mathrm{Ext}|} \prod_{i=1}^{n} \widetilde{z}(\Gamma_i) e^{2d\kappa e^{-\widetilde{\alpha}+1} L(\Gamma_i)} \widetilde{\mathcal{Z}}(\mathrm{Int}) e^{\widetilde{s}|\mathrm{Int}|} \\ &\leqslant e^{-\widetilde{s}|\Lambda|} \sum_{\{\Gamma_1,...,\Gamma_n\}_{\mathrm{ext}}} \prod_{i=1}^{n} \widetilde{z}(\Gamma_i) e^{(2d\kappa e^{-\widetilde{\alpha}+1}+\widetilde{s}) L(\Gamma_i)} \widetilde{\mathcal{Z}}(\mathrm{Int}) \\ &\leqslant e^{-\widetilde{s}|\Lambda|} \widetilde{\mathcal{Z}}(\mathrm{Int}),\end{aligned}$$

where in the last inequality, we used $\widetilde{s} \leqslant \kappa e^{-\widetilde{\alpha}+1}$. This gives (6.18) using again the estimates (3.17). ∎

This ends the proof of Proposition 1.

We now come back to the proof of Theorem 2. We put $\mu_1(t) = \mu_1 + t$, $\mu_2(t) = \mu_2 + t$ with $e^{\mu_1} + e^{\mu_2} = 1$. Then, by definitions (3.9),(3.10) and (6.7), we have

$$\begin{aligned} a_{\mathrm{emp}} - a_{\mathrm{mixt}} &= p_{\mathrm{mixt}} - p_{\mathrm{emp}} = t + \ln(e^{\mu_1} + e^{\mu_2}) \\ &\quad + \lim_{\Lambda \uparrow \mathbb{Z}^d} \frac{1}{|\Lambda|} \left[\ln \mathcal{Z}_{\mathrm{mixt}}(\Lambda) - \ln \mathcal{Z}_{\mathrm{emp}}(\Lambda) \right], \end{aligned} \tag{6.29}$$

where

$$\mathcal{Z}_q(\Lambda) = e^{-g_q|\Lambda|} \Xi'_q(\Lambda) = \sum_{\{\Gamma_1,...,\Gamma_n\}_{\mathrm{comp}}} \prod_{i=1}^{n} z'_q(\Gamma_i). \tag{6.30}$$

The function $t + \ln(e^{\mu_1} + e^{\mu_2}) = t$ is obviously increasing, negative for $t < 0$, positive for $t > 0$, and it intersects the horizontal coordinate axis only at one point $t=0$. The difference $a_{\mathrm{mixt}}-a_{\mathrm{emp}}$ will satisfy the same properties with the intersecting point slightly changed) provided

$$\frac{1}{|\Lambda|}\left|\frac{\partial}{\partial t}\ln \mathcal{Z}_{\mathrm{emp}}(\Lambda)-\frac{\partial}{\partial t}\ln \mathcal{Z}_{\mathrm{mixt}}(\Lambda)\right|<1 \tag{6.31}$$

uniformly in Λ.

Let us first give an upper bound on the derivative $\frac{\partial}{\partial t}z'_q(\Gamma)$ of the truncated activity. By virtue of relations (3.8),(3.6) one gets for every stable q-contour Γ, that either $\frac{\partial}{\partial t}z'_q(\Gamma)=0$, or:

$$\begin{aligned}\left|\frac{\partial}{\partial t}z'_q(\Gamma)\right| &= \left|\frac{\partial}{\partial t}\ln\omega(\Gamma)-\frac{\partial}{\partial t}g_q(\Gamma)+\frac{\partial}{\partial t}\ln\frac{\Xi_m(\mathrm{Int}_m\,\Gamma)}{\Xi_q(\mathrm{Int}_m\,\Gamma)}\right|z'_q(\Gamma)\\ &\leqslant (1+|\mathrm{Int}_m\,\Gamma|)z'_q(\Gamma)\leqslant |V(\Gamma)|e^{-\alpha|L(\Gamma)|}.\end{aligned} \tag{6.32}$$

On the other hand,

$$\left|\frac{1}{|\Lambda|}\frac{\partial}{\partial t}\ln \mathcal{Z}_q(\Lambda)\right|\leqslant \sum_{\Gamma:\mathrm{supp}\,\Gamma\ni x}\left|\frac{\partial}{\partial t}z'_q(\Gamma)\right|\times\left|\frac{\mathcal{Z}_q(\Lambda\setminus\{\Gamma\})}{\mathcal{Z}_q(\Lambda)}\right|. \tag{6.33}$$

Here the sums are over contours Γ containing a given point x and

$$\mathcal{Z}_q(\Lambda\setminus\{\Gamma\})=\sum^{*}_{\{\Gamma_1,\dots,\Gamma_n\}_{\mathrm{comp}}} z'_q(\Gamma), \tag{6.34}$$

where the sum goes over all families $\{\Gamma_1,\dots,\Gamma_n\}_{\mathrm{comp}}$ compatible with Γ. This sum can be bounded using the cluster expansion. Indeed, denoting $\overline{S}$ the set of sites at distance less or equal to 1 from the support of Γ, we get by (3.13) and (3.17):

$$\begin{aligned}\frac{\mathcal{Z}_q(\Lambda\setminus\{\Gamma\})}{\mathcal{Z}_q(\Lambda)} &= \exp\left\{-\sum_{X:\mathrm{supp}X\cap\overline{S}=\emptyset}\Phi_q(X)\right\}\leqslant \exp\left\{|\overline{S}|\sum_{X:\mathrm{supp}\,X\ni x}\left|\Phi_q(X)\right|\right\}\\ &\leqslant \exp\left\{(2d+1)|S(\Gamma)|\kappa e^{-\alpha}\right\}\leqslant \exp\left\{(2d+1)L(\Gamma)\kappa e^{-\alpha}\right\}.\end{aligned} \tag{6.35}$$

Inserting this bound in (6.33) and taking into account the inequality (6.32) and the estimate

$$|V(\Gamma)|\leqslant |S(\Gamma)|\mathrm{diam}\,\Gamma\leqslant |S(\Gamma)|^2\leqslant e^{|S(\Gamma)|}\leqslant e^{L(\Gamma)}.$$

gives

$$\left|\frac{1}{|\Lambda|}\frac{\partial}{\partial t}\ln \mathcal{Z}_q(\Lambda)\right| \leqslant \sum_{\Gamma:\mathrm{supp}\,\Gamma\ni x} e^{-\alpha L(\Gamma)+(2d+2)L(\Gamma)Ke^{-\alpha}} \leqslant \sum_{n\geqslant 1} \nu^n e^{-\alpha n} e^{2(d+1)\kappa e^{-\alpha} n}.$$

Using that $\kappa \simeq 4.9\nu$, we get that for $2(d+1)\kappa e^{-\alpha} \leqslant 1$ this last sum is less than $1/2$. This implies (6.31) ending the proof of Theorem 2. ∎

7. PROOF OF THEOREM 3

Let us first explain the idea of the proof.

In dimension $d=3$, the first excitation of a flat interface is obtained by replacing an empty site of the interface by an occupied one (denote $I_{\mathrm{el}}^{\mathrm{up}}$ such an interface) or by replacing an occupied site of the interface by an empty one (denote $I_{\mathrm{el}}^{\mathrm{down}}$ such an interface). In the first case, we have

$$\begin{aligned}
&\sum_{\substack{I:\mathrm{supp}\ I\subset \overline{V}\\ \mathrm{supp}\ I=\mathrm{supp}\ I_{\mathrm{el}}^{\mathrm{up}}}} \omega(I) e^{-p(\mu_1^*,\mu_2^*)|S(I)|}\\
&= \sum_{n=0}^{N-1} \binom{N-1}{n} \frac{e^{(\mu_1^*-\beta J_1)n} e^{-(\mu_2^*-\beta J_2)(N-1-n)}}{e^{p(\mu_1^*,\mu_2^*)N}} (e^{\mu_1^*-5\beta J_1}+e^{\mu_2^*-5\beta J_2})\\
&= (c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2})^N \frac{c_1^* e^{-5\beta J_1}+c_2^* e^{-5\beta J_2}}{c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2}}.
\end{aligned}$$

In the second case we have

$$\begin{aligned}
&\sum_{\substack{I:\mathrm{supp}\ I\subset \overline{V}\\ \mathrm{supp}\ I=\mathrm{supp}\ I_{\mathrm{el}}^{\mathrm{down}}}} \omega(I) e^{-p(\mu_1^*,\mu_2^*)|S(I)|}\\
&= \sum_{n=0}^{N-4} \frac{\binom{N-4}{n} e^{(\mu_1^*-\beta J_1)n} e^{-(\mu_2^*-\beta J_2)(N-4-n)}}{e^{p(\mu_1^*,\mu_2^*)N}}\\
&\quad \times \sum_{m=1}^{4} \binom{4}{m} e^{2m(\mu_1^*-\beta J_1)} e^{-(8-2m)(\mu_2^*-\beta J_2)}\\
&= (c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2})^N \frac{(c_1^* e^{-2\beta J_1}+c_2^* e^{-2\beta J_2})^4}{(c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2})^4}.
\end{aligned}$$

In dimension $d=2$, the first excitation of a flat interface is obtained by splitting it into a left part and a right part and then shift the right part by a height 1 or -1 (denote I_{el} such an interface). Then, we have

$$\begin{aligned}
&\sum_{\substack{I:\text{supp } I\subset\overline{V}\\ \text{supp } I=\text{supp } I_{\text{el}}}} \omega(I)e^{-p(\mu_1^*,\mu_2^*)|S(I)|}\\
&=\sum_{n=0}^{N-1}\binom{N-m}{n}\frac{e^{(\mu_1^*-\beta J_1)n}e^{-(\mu_2^*-\beta J_2)(N-m-1)}}{e^{p(\mu_1^*,\mu_2^*)N}}(e^{\mu_1^*-2\beta J_1}+e^{\mu_2^*-2\beta J_2})\\
&=(c_1^*e^{-\beta J_1}+c_2^*e^{-J_2})^N\frac{c_1^*e^{-2\beta J_1}+c_2^*e^{-2\beta J_2}}{c_1^*e^{-\beta J_1}+c_2^*e^{-\beta J_2}}.
\end{aligned}$$

Note, that in fact such modified interfaces are not allowed with the boundary condition $\chi^{\text{mixt,emp}}$. However, one can lightly modify this boundary condition to allow such interface, leaving the resulting surface tension unchanged.

To study the difference $F'(\overline{V})-F_{\text{flat}}(\overline{V})$, we shall express the quantity

$$(c_1^*e^{-\beta J_1}+c_2^*e^{-\beta J_2})^{-N}\sum_{I:\text{supp } I\subset\overline{V}}\omega(I)e^{-p(\mu_1^*,\mu_2^*)|S(I)|}$$

as the partition function of a gas of excitations to be called walls or more generally aggregates with small activities at low enough temperature.

This will allow us to exponentiate this quantity and to obtained that the difference $(F'(\overline{V})-F'_{\text{flat}}(\overline{V}))/N$ can be expressed as a convergent series (up to a boundary term) whose leading terms are:

$$-\frac{1}{\beta}\frac{c_1^*e^{-5\beta J_1}+c_2^*e^{-5\beta J_2}}{c_1^*e^{-\beta J_1}+c_2^*e^{-\beta J_2}}-\frac{1}{\beta}\frac{(c_1^*e^{-2\beta J_1}+c_2^*e^{-2\beta J_2})^4}{(c_1^*e^{-\beta J_1}+c_2^*e^{-\beta J_2})^4}$$

in three-dimensions and

$$-\frac{2}{\beta}\frac{c_1^*e^{-2\beta J_1}+c_2^*e^{-2\beta J_2}}{c_1^*e^{-\beta J_1}+c_2^*e^{-\beta J_2}}$$

in two-dimensions.

7.1. Decorated Interfaces

The first step is to express the quantity $A(I)$ defined by (4.9) in a form suitable for our purpose. We write for each support of the mixt or emp cluster C in $A(I)$:

$$e^{-\tilde{\Phi}_{\mathrm{mixt}}(C)\frac{|C\cap D|}{|C|}} = 1 + (e^{-\tilde{\Phi}_{\mathrm{mixt}}(C)\frac{|C\cap D|}{|C|}} - 1) \equiv 1 + \tilde{\psi}_{\mathrm{mixt}}(C),$$
$$e^{-\tilde{\Phi}_{\mathrm{emp}}(C)\frac{|C\cap U|}{|C|}} = 1 + (e^{-\tilde{\Phi}_{\mathrm{emp}}(C)\frac{|C\cap U|}{|C|}} - 1) \equiv 1 + \tilde{\psi}_{\mathrm{emp}}(C).$$

Define for a connected family A of support of clusters:

$$\tilde{\psi}_{\mathrm{mixt}}(A) = \prod_{C\in A} \tilde{\psi}_{\mathrm{mixt}}(C), \quad \tilde{\psi}_{\mathrm{emp}}(A) = \prod_{C\in A} \tilde{\psi}_{\mathrm{emp}}(A).$$

Then

$$\begin{aligned} A(I) &= \prod_{C\cap S(I)\neq\emptyset} e^{-\tilde{\Phi}_{\mathrm{mixt}}(C)\frac{|C\cap D|}{|C|}} \prod_{C'\cap S(I)\neq\emptyset} e^{-\tilde{\Phi}_{\mathrm{emp}}(C')\frac{|C'\cap U|}{|C|}} \\ &= \sum_{\{A_1,\dots,A_n\}_{\mathrm{comp}}:A_i\cap S(I)\neq\emptyset} \prod_{i=1}^{n} \tilde{\psi}_{\mathrm{mixt}}(A_i) \sum_{\{A_1,\dots,A_m\}_{\mathrm{comp}}:A_i\cap S(I)\neq\emptyset} \prod_{j=1}^{m} \tilde{\psi}_{\mathrm{emp}}(A_j), \end{aligned}$$

where the sums are over compatible families of connected sets A_i of support of clusters touching the interface. As it was done for multi-indexes, it is convenient to sum all A with the same support say $\mathcal{D}$ to be called decoration. We define the weight

$$\psi_{\mathrm{mixt}}(\mathcal{D}) = \sum_{A:\mathrm{supp}\,A=\mathcal{D}} \tilde{\psi}_{\mathrm{mixt}}(A) = \sum_{\{C_1,\dots,C_n\}:\cup C_i=\mathcal{D}} \prod_{i=1}^{n} \tilde{\psi}_{\mathrm{mixt}}(C_i), \tag{7.1}$$

$$\psi_{\mathrm{emp}}(\mathcal{D}) = \sum_{A:\mathrm{supp}\,A=\mathcal{D}} \tilde{\psi}_{\mathrm{emp}}(A) = \sum_{\{C_1,\dots,C_n\}:\cup C_i=\mathcal{D}} \prod_{i=1}^{n} \tilde{\psi}_{\mathrm{emp}}(C_i). \tag{7.2}$$

This leads to

$$\begin{aligned} e^{-\beta F'(\overline{V})} = &\sum_{I:\mathrm{supp}\ I\subset\overline{V}} \omega(I) e^{-p(\mu_1^*,\mu_2^*)|S(I)|} \sum_{\substack{\{\mathcal{D}_1,\dots,\mathcal{D}_n\}\mathrm{comp}:\\ \mathcal{D}_i\cap S(I)\neq\emptyset,\mathcal{D}_i\cap D\neq\emptyset}} \prod_{i=1}^{n} \psi_{\mathrm{mixt}}(\mathcal{D}_i) \\ &\times \sum_{\substack{\{\mathcal{D}_1,\dots,\mathcal{D}_m\}\mathrm{comp}:\\ \mathcal{D}_i\cap S(I)\neq\emptyset,\mathcal{D}_i\cap U\neq\emptyset}} \prod_{j=1}^{m} \psi_{\mathrm{emp}}(\mathcal{D}_j), \end{aligned} \tag{7.3}$$

where the sums are over compatible families of decorations touching the interface.

We define a decorated interface as a triplet $I^{\mathrm{de}}=\{I,\mathfrak{D}_{\mathrm{mixt}},\mathfrak{D}_{\mathrm{emp}}\}$, where I is an interface, $\mathfrak{D}_{\mathrm{mixt}}$ is a collection of mixt-decorations touching the interface and $\mathfrak{D}_{\mathrm{emp}}$ is a collection of emp-decorations touching the interface.

The weights of decorations may be controlled with the inequalities $|e^{-\tilde{\Phi}_{\mathrm{mixt}}(C)\frac{|C\cap D|}{|C|}}-1|\leqslant(e-1)|\tilde{\Phi}_{\mathrm{mixt}}(C)|$ and $|e^{-\tilde{\Phi}_{\mathrm{emp}}(\mathcal{D})\frac{|C\cap U|}{|C|}}-1|\leqslant(e-1)|\tilde{\Phi}_{\mathrm{emp}}(\mathcal{D})|$. Together with (4.11), this implies the bounds (see ref. 29):

$$|\psi_{\mathrm{mixt}}(\mathcal{D})|\leqslant(8e(e-1)\kappa e^{-\alpha})^{L(\mathcal{D})},\tag{7.4}$$

$$|\psi_{\mathrm{emp}}(\mathcal{D})|\leqslant(8e(e-1)\kappa e^{-\alpha})^{L(\mathcal{D})}.\tag{7.5}$$

7.2. Walls and Aggregates

We now introduce the notion of walls and aggregates by the following definitions.

Consider a decorated interface $I^{\mathrm{de}}=\{I,\mathfrak{D}_{\mathrm{mixt}},\mathfrak{D}_{\mathrm{emp}}\}$. Let Π_0 denote the horizontal hyper-plane $x_d=0$ and let π denote the projection parallel to the vertical axis on this hyper-plane: $\pi(x_1,...,x_d)=(x_1,...,x_{d-1})$, $\pi(A)=\cup_{x\in A}\pi(x)$. A pair $\{s_x,s_y\}$ of the interface I is called correct if

(1) $\pi(x)=\pi(y)$ (the bond xy is vertical);

(2) there is no other pair pairs $\{s_{x'},s_{y'}\}$ of the interface such that $\pi(x')=\pi(x)$;

(3) there are no decorations such that $\pi(\mathcal{D})\supset\pi(x)$.

The connected components of the set of correct pairs are called *ceilings* and denoted $\mathcal{C}$. The connected components of the set of noncorrect pairs are called *walls* (see Fig. 6).

For a wall W, we use $S_\alpha(W)$ to denote the set of sites for which $s_x=\alpha$. The set supp $W=S_0(W)\cup S_1(W)\cup S_2(W)$ is called support of the wall W. As for the contours and the interfaces, we will also use $S(W)=S_1(W)\cup S_2(W)$ to denote the set of occupied sites of the wall, $L_1(W)$ (respectively $L_2(W)$) to denote the number of nearest-neighbor pairs $\langle x,y\rangle$ such that $s_x=1$ and $s_y=0$ (respectively, $s_x=2$ and $s_y=0$) and $L(W)=L_1(W)+L_2(W)$.

Denote further $\mathcal{W}(I)$ the set of walls of the interface I.

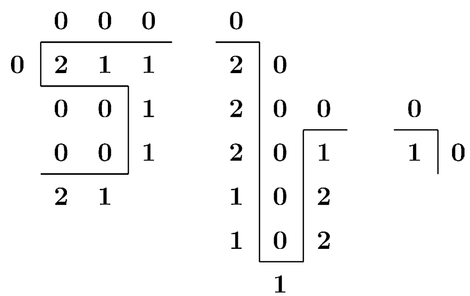

Fig. 6. The walls corresponding to the interface of Fig. 4.

The union $\cup_{W\in\mathcal{W}(I)}\text{supp } W \cup_{\mathcal{D}\in I^{\text{de}}} \mathcal{D}$ split into maximal connected components called aggregates. Namely, an aggregate w of a decorated interface is a family

$$w=\{W_1, ..., W_n; \mathcal{D}_1, ..., \mathcal{D}_m\}$$

such that the set $\cup_{i=1}^{n}\text{supp } W_i \cup_{j=1}^{m} \mathcal{D}_j$ is connected.

A collection of aggregates $\{w_1, \ldots, w_n\}$ is called *admissible* if there exists a decorated interface I^{de} such that $w_1, \ldots, w_n$ are the aggregates of I^{de}.

Here comes a difference for definitions between dimensions 2 and 3.

In three dimensions an aggregate is called a *standard aggregate*, (or aggregate in standard position), if there exits a decorated interface I^{de} such that w is the unique aggregate of I^{de}. To any aggregate w, we can associate a unique standard aggregate which is just a translate of w. In this way, one can associate to any admissible collection of aggregates a unique collection of standard aggregates. Such collections are called admissible collections of standard aggregates. To an admissible collection of standard aggregates we can associate in a unique way an admissible collection of aggregates.

7.3. Expansions

With these definitions and notations, one gets from (7.3), the following expansion

$$e^{-\beta F'(\overline{V})}=(c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2})^N \sum_{\{w_1,\ldots,w_n\}_{\text{adm}}} \prod_{i=1}^{n} z(w_i), \tag{7.6}$$

where the sum is over admissible collections of standard aggregates and the activities of aggregates are given by

$$z(w)=\prod_{W\in w}\frac{e^{-\beta J_1 L_1(W)-\beta J_2 L_2(W)+\mu_1^*|S_1(W)|+\mu_2^*|S_2(W)|}}{e^{p(\mu_1^*,\mu_2^*)|S(W)|}(c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2})^{|\pi(W)|}}\prod_{\mathcal{D}\in w}\psi(\mathcal{D}). \tag{7.7}$$

Here $\psi(\mathcal{D})=\psi_{\text{mixt}}(\mathcal{D})$ for the mixt-decorations and $\psi(\mathcal{D})=\psi_{\text{emp}}(\mathcal{D})$ for the emp-decorations.

In two-dimensions we proceed differently. For an aggregate w, we consider the ceiling components to the left and to the right of w, respectively, denoted $\mathcal{C}^{(L)}$ and $\mathcal{C}^{(R)}$. Let $h^{(L)}$ (respectively, $h^{(R)}$) be the second coordinate of any empty site of $\mathcal{C}^{(L)}$ (respectively, $\mathcal{C}^{(R)}$). We define the position $p(w)$ of th aggregate w as $p(w)=h^{(L)}$ and the height of the aggregate w as $h(w)=h^{(R)}-h^{(L)}$. An aggregate w is now called standard aggregate (or aggregate in standard position) if $p(w)=0$. One obviously can associate to any aggregate an aggregate in standard position and to any admissible collection of aggregates a unique collection of standard aggregates. As before such collections are called admissible collections of standard aggregates and to an admissible collection of standard aggregates we can associate a unique admissible collection of aggregates.

For an admissible collection of aggregates $\{w_1',\ldots,w_n'\}_{\text{adm}}$, one has the constraint $\sum_{i=1}^n h(w_i')=0$. If we let, for $i=1,\ldots,n$, w_i denote the standard aggregates corresponding to w_i', this constraint reads also $\sum_{i=1}^n h(w_i)=0$. From (7.3), we then get:

$$e^{-\beta F'(\overline{V})}=(c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2})^N\sum_{\{w_1,\ldots,w_n\}_{\text{adm}}}\prod_{i=1}^n z(w_i)\delta\Big(\sum_{i=1}^n h(w_i),0\Big), \tag{7.8}$$

where the activities $z(w)$ of aggregates are also given by (7.7).

We now introduce the notion of *elementary walls* which are the walls corresponding to the elementary interfaces mentioned in the beginning of this section.

In two-dimensions, an elementary wall W_{el} is a wall that contains two pairs $\{s_x,s_y\}$ and $\{s_x,s_z\}$ such that the site x is occupied, the sites y and z are empty, y is above x and z is to the left or to the right of x.

The activity of such a wall are easily computed and we have

$$\sum_{W_{\text{el}}:\text{supp}W_{\text{el}}=\{x,y,z\}} z(W_{\text{el}})=\frac{c_1^* e^{-2\beta J_1}+c_2^* e^{-2\beta J_2}}{c_1^* e^{-\beta J_1}+c_2^* e^{-\beta J_2}}. \tag{7.9}$$

In three-dimensions, we call elementary wall, either a wall (corresponding to the elementary interface $I_{\rm el}^{\rm up}$) that contains four pairs $\{s_x, s_{x_i}\}$, $i = 1, \ldots, 4$, such that the site x is occupied, the sites x_i are empty and all the sites leave on the plane $x^3 = 0$, or a wall (corresponding to the elementary interface $I_{\rm down}^{\rm up}$) that contains eight pairs $\{s_x, s_{x_i}\}$, $\{s_{x_i}, s_{y_i}\}$, $i = 1, \ldots, 4$, such that the sites x and z_i are empty, the sites y_i are occupied, the sites x and x_i leaves on the plane $x^3 = -1$, the sites y_i leaves on the plane $x^3 = 0$.

In the first case we have

$$\sum_{W_{\rm el}:{\rm supp}W_{\rm el}=\{x,x_1,x_2,x_3,x_4\}} z(w_{\rm el}) = \frac{c_1^* e^{-5\beta J_1} + c_2^* e^{-5\beta J_2}}{c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2}}, \tag{7.10}$$

while in the second case

$$\sum_{W_{\rm el}:{\rm supp}W_{\rm el}=\{x,x_1,x_2,x_3,x_4,y_1,y_2,y_3,y_4\}} z(w_{\rm el}) = \frac{(c_1^* e^{-2\beta J_1} + c_2^* e^{-2\beta J_2})^4}{(c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2})^4}. \tag{7.11}$$

For nonelementary walls and aggregates, the activities (7.7) may be bounded as

$$z(w) \leqslant \frac{(a_g e^{-\beta J})^{L(w)}}{(c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2})^{|\pi(w)|}}, \tag{7.12}$$

$$\sum_{w:L(w)=L} z(w) \leqslant \frac{(a_g e^{-\beta J})^{L}}{(c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2})^{|\pi(w)|}}, \tag{7.13}$$

where

$$a_g = \begin{cases} 8e(e-1)\kappa e^{-\alpha} e^{\beta J} & \text{if } L(w) \geqslant 2d, \\ 1 & \text{otherwise.} \end{cases}$$

This allows to exponentiate the partitions functions of the gas of aggregates in the RHS of (7.6) and (7.8), for low enough temperatures. We define multi-indexes Y corresponding to aggregates as function from the set of aggregates into the set of non negative integers, and we let ${\rm supp}\, Y = \cup_{w:Y(w)\geqslant 1} {\rm supp}\, w$. The truncated functional corresponding to the activities z is given by

$$\Psi(w) = \frac{a(Y)}{\prod_w Y(w)!} \prod_w z(w)^{Y(w)}, \tag{7.14}$$

where the factor $a(Y)$ is defined as in (3.12). Then

$$\sum_{\{w_1,\dots,w_n\}_{\mathrm{adm}}} \prod_{i=1}^{n} z(w_i) = \exp\Big\{ \sum_{Y:\mathrm{supp}\ Y\subset\overline{V}} \Psi(Y)\Big\} = e^{-\beta N\mathcal{F}+\sigma(\overline{V}|\Psi)} \tag{7.15}$$

in three dimensions and

$$\begin{aligned}\sum_{\{w_1,\dots,w_n\}_{\mathrm{adm}}} \prod_{i=1}^{n} z(w_i)\delta\Big(\sum_{i=1}^{n} h(w_i),0\Big) &= \Pr\Big\{\sum_{i=1}^{n} h(w_i)=0\Big\}\exp\Big\{\sum_{Y:\mathrm{supp}\ Y\subset\overline{V}} \Psi(Y)\Big\}\\ &= \Pr\Big\{\sum_{i=1}^{n} h(w_i)=0\Big\} e^{-\beta N\mathcal{F}+\sigma(\overline{V}|\Psi)}\end{aligned} \tag{7.16}$$

in two dimensions. Here

$$-\beta\mathcal{F} = \sum_{Y:\mathrm{supp}Y\ni 0} \frac{\Psi(Y)}{|\mathrm{supp}\ Y\cap\Pi_0|}, \tag{7.17}$$

$$\sigma(\overline{V}\mid\Psi) = -\sum_{Y:\mathrm{supp}\ Y\cap\overline{V}^c\neq\emptyset} \Psi(Y)\frac{|\mathrm{supp}\ Y\cap\pi(\overline{V})|}{|\mathrm{supp}\ Y\cap\Pi_0|} \tag{7.18}$$

and

$$\Pr\Big\{\sum_{i=1}^{n} h(w_i)=0\Big\} = \frac{\sum_{\{w_1,\dots,w_n\}_{\mathrm{adm}}} \prod_{i=1}^{n} z(w_i)\delta\Big(\sum_{i=1}^{n} h(w_i),0\Big)}{\sum_{\{w_1,\dots,w_n\}_{\mathrm{adm}}} \prod_{i=1}^{n} z(w_i)}. \tag{7.19}$$

The series (7.17) converges whenever $8e(e-1)\kappa^2 e^{-\alpha}<1$. This can be seen by verifying the convergence condition (6.2) with the activities $z(w)$ and with the contours replaced by aggregates.

Notice that the multi-indexes involved in the sum of (7.18) intersects both $\pi(\overline{V})$ and $\overline{V}^c=\mathbb{Z}^d\setminus\overline{V}$. Thus at low temperatures, this sum can be bounded by L^{d-2} times a constant so that this term will give no contribution to the surface tension in the thermodynamic limit. In addition, the probability $\Pr\{\sum_{i=1}^{n} h(w_i)=0\}$, may be controlled by known techniques (see e.g. refs. 11, 30–32) and

$$\lim_{L\to\infty}(1/N)\ln\Pr\Big\{\sum_{i=1}^{n} h(w_i)=0\Big\}=0.$$

Hence, by taking the thermodynamic limit $L \to \infty$ in Eqs. (7.6) and (7.8) we obtain:

$$e^{-\beta(\tau_{\text{mixt,emp}} - \mathcal{F})} = c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2}. \tag{7.20}$$

Whenever a multi-index Y contains only one aggregate w ($Y(w) = 1$ and $Y(w') = 0$ for $w' \neq w$) one has $\Psi(Y) = z(w)$. The leading terms of $\mathcal{F}$ are then obtained with the help of relations (7.9)–(7.11). This gives the expressions (5.5) and (5.6). Taking furthermore into account the expression (4.16) ends the proof of the theorem.

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