

Interfacial tensions for binary mixtures versus Solid-On-Solid models.

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Abstract

The quenched and annealed disorder are introduced within the problem of interfacial tension for binary mixtures using the $d = 2$ Solid-On-Solid model. New formulae for surface tension of mixture of molecules are derived. Exact expressions for γ^{annealed} and for γ^{quenched} as a function of the mole fraction c are obtained for ideal and regular mixtures and interpreted in terms of the mobility of the molecules at the interface.

Key words : Interfacial tensions, Solutions, Regular solutions, Ideal solutions, SOS model

PACS numbers : 05.20.-y,68.10.Cr,05.50.+q

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1 Introduction

Interfacial tensions play a key role in surface phenomena and, up to our knowledge, no theory leads to a good prediction of the behaviour of these quantities in terms of atomic interactions.

Several approaches have been so far developed : the radial theory in which the interfacial tension is expressed in terms of the distribution function [1], the lattice approach in which the interfacial tension is expressed in terms of ratios of partition functions [2], phenomenological and mean field models supported by numerical simulations [3, 4] and numerous numerical and experimental data [5] are also available.

Among this interesting problem, not only for theoretical purpose, one of the open problem is to predict the surface tension for a binary mixture combining two types of liquid-vapour and/or liquid-liquid interfaces A/C and B/C as schematically reproduced in Fig. 1.

INSERT HERE FIGURE 1

For immiscible fluids, some approximate formulae have been derived using thermodynamics and statistical mechanics [6] leading to relations between the liquid-liquid interfacial tension and the liquid-vapour surface tension. Among them, we should quote for convenience the empirical Antonov's rule [7]

$$\gamma_{A/B} = |\gamma_A - \gamma_B| \quad (1)$$

between the interfacial tension $\gamma_{A/B}$ and the surface tensions γ_A, γ_B with their common vapour; and the classical formula based on the geometric average [8]

$$\gamma_{A/B} = \gamma_A + \gamma_B - 2K\sqrt{\gamma_A\gamma_B} \quad (2)$$

between the interfacial tension and the pure liquid surface tensions, where K is a constant depending on the nature of the system.

For miscible liquids, say A and B , the problem is to discuss how the interfacial tension $\gamma_{AB/C}$ will depend on the composition of A or B in the bulk in contact with C . Using thermodynamical considerations for perfect solutions, several equations corresponding to this type of mixture have been derived in the literature [9, 10, 11]. For molecules of similar size, it is for instance known that

$$e^{-\beta a \gamma_{AB/C}} = c.e^{-\beta a \gamma_{A/C}} + (1 - c).e^{-\beta a \gamma_{B/C}} \quad (3)$$

where the γ 's denote the interfacial tensions, c is the fixed molar fraction of A in the AB mixture and a is the mean surface area per molecule. Another well known formula can be obtained whenever $\gamma_{A/C}$ and $\gamma_{B/C}$ are sufficiently close to each other [11]

$$\gamma_{AB/C} = c.\gamma_{A/C} + (1 - c).\gamma_{B/C} \quad (4)$$

For non-ideal solutions, we still refer to the Guggenheim's formula based on a quasi-crystalline model [10] and to the Defay, Prigogine and co-workers development [11] which is also based on a lattice approximation.

The Guggenheim's result, which assumes that the interface is composed by a single layer, is given by:

$$e^{-\beta a \gamma_{AB/C}} = c.e^{-\beta a \gamma_{A/C}} e^{\beta m \omega (1-c)^2} + (1 - c).e^{-\beta a \gamma_{B/C}} e^{\beta m \omega c^2}, \quad (5)$$

where m is a constant depending on the lattice structure and ω is the Guggenheim interaction energy describing the interaction energy between the molecules of two different types A and B .

The Defay, Prigogine and co-workers' formula [11], which is derived for a monolayer model, can be written as:

$$\gamma_{AB/C} = \gamma_{A/C} + RT \log \frac{x_1^m}{x_1^l} + \alpha l [(x_2^m)^2 - (x_2^l)^2] - \alpha m (x_2^l)^2 \quad (6)$$

$$= \gamma_{B/C} + RT \log \frac{x_2^m}{x_2^l} + \alpha l [(x_1^m)^2 - (x_1^l)^2] - \alpha m (x_1^l)^2 \quad (7)$$

This model describes a liquid like a stack of molecule planes. Each molecule is situated in a plane parallel to the liquid surface and surrounded by z neighbours of which lz are in the same plane and mz in each of the adjacent planes, with $l + 2m = 1$. The interface with C is viewed as one layer of molecules, each of which has $(l + m)z$ nearest neighbours. The variables x_1 and x_2 denote the mole fractions of liquid 1 (A) and 2 (B) respectively (the notation l and m are indexes for quantities corresponding to the liquid phase and to the surface phase regarded as a monolayer resp.). Recalling that these equations were first derived by Schuchowitsky [12] and by Guggenheim [10], we can obtain the equation (5) from (7) knowing that: $\omega/z = \alpha/z = N[\epsilon_{12} - \frac{\epsilon_{11} + \epsilon_{22}}{2}]$, where z is the number of nearest neighbours, N the Avogadro's number, α and ω are the excess of potential energy of an AB pair of neighbours in comparison with the mean of the energies of a AA and a BB pair, and replace x_1^m by x_1^l in the α -terms assumed to be small.

More than one layer cases have been considered in the literature, from two layers [13] to the multilayer models [14] where it has been shown that, as the number of transition layers between the surface and solution tends to

infinity, the model becomes perfectly consistent with the Gibbs adsorption equation.

This monolayer model, even though being a first approximation, leads however to some good comparison with experimental data.

These approaches consider nevertheless a flat and very rigid interface between the two media A and C . The validity of this kind of approximation is obviously questionable at a microscopic scale and could be important for long chain molecules such as polymers for which the entropy of configuration can be very large. The purpose of this paper is to reconsider this problem of binary mixtures within a microscopic model where the interfaces can fluctuate, as represented in Fig. 2, and where exact expressions can be derived for $\gamma_{AB/C}$ even for interacting molecules A and B .

INSERT HERE FIGURE 2

This kind of results complements thus other approaches based on thermodynamical hypothesis about the behaviour of the local density and on microscopic simulations [4].

This category of models where it is possible to compute exactly the interfacial tensions for mixtures is the disordered generalization of the so-called Solid-On-Solid (SOS) models.

In Section 2, we give a simple microscopic derivation of the formulae for the interfacial tension of mixtures (4) and (5) within Solid-On-Solid models. This allows us to calculate explicitly interfacial tensions and to apply our method to perfect, ideal or dilute solutions in the sense of Guggenheim [10]. Let us also mention that this approach can easily be extended to the coexistence of more than two different liquids. More general cases for interacting

molecules are considered in Section 3 and concluding remarks are presented in Section 4.

2 The ideal case

2.1 The Solid-On-Solid (SOS) model

The SOS model has been introduced by Buff, Lovett and Stillinger [15] to describe the interface between two media using a gaussian approximation. This model represents a media A in equilibrium with a media C . The corresponding A/C interface may be described by a collection of heights $h_0, h_1, \dots, h_N \in \mathbb{R}$ assuming no overhangs. A typical configuration is given in the Fig. 3.

INSERT HERE FIGURE 3

We present here the $d = 2$ SOS model. For simplicity, we consider that the energetic cost of the interface is proportional to its length. The energetic cost of the interface is thus given by

$$H(h_0 \cdots h_N) = J_{AC} \sum_{i=0}^{N-1} [1 + |h_{i+1} - h_i|] \quad (8)$$

where J_{AC} represents the energetic cost per unit length for the A/C interface. The associated density of free-energy or interfacial tension is then given for a flat interface by

$$\gamma_{A/C} = -\frac{1}{\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \log Z(N, \beta) \quad (9)$$

where $Z(N, \beta)$ is the partition function corresponding to a flat interface

$$Z(N, \beta) = \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N e^{-\beta J_{AC} \sum_{i=0}^{N-1} (1+|h_{i+1}-h_i|)} \delta(h_0 - 0) \delta(h_N - 0) \quad (10)$$

In this paper we will use the disordered generalization of this model. That means that the energetic cost J_{AC} is no more a constant but a random variable which can take different values.

To model the interface for binary mixtures, we consider that the coupling per unit length is also a random variable J . This variable may take two values J_{AC} and J_{BC} with probabilities c and $1 - c$ where, as previously mentioned, c is physically the mole fraction of A in the bulk of the AB mixture. This allows us to represent the interface by two N -uples of independent random variables (h_0, \dots, h_N) and (J_0, \dots, J_N) . In this way, the interface can adjust its height h and, by moving or not molecules, also the corresponding energetic cost J taking into account the fixed concentration c . In this approach the molecules of the mixture are not distinguishable and have similar size. Each site i is occupied by one molecule.

The energetic cost of this interface is given by the Hamiltonian

$$H(h_0 \cdots h_N) = \sum_{i=0}^{N-1} J_i [a + |h_{i+1} - h_i|] \quad (11)$$

where J_i may take the value J_{AC} or J_{BC} with probability c or $1 - c$ and a is the reference unit length. The associated partition function is given by

$$Z(J_0, J_1, \dots, J_{N-1}) = \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N e^{-\beta \sum_{i=0}^{N-1} J_i (a + |h_{i+1} - h_i|)} \delta(h_0) \delta(h_N). \quad (12)$$

It is well known that random systems are often related to disordered systems for which one has introduced the notion of quenched and annealed

disorder [16]. For the annealed case, the couplings are considered to be random and will be treated in the same way than the heights. For the quenched disorder, the couplings are frozen in a given configuration. There are then two ways to define the associated free energy density

$$\gamma_{AB/C}^{\text{quenched}} = -\frac{1}{a\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \langle \log Z(J_0, J_1, \dots, J_{N-1}) \rangle \quad (13)$$

and

$$\gamma_{AB/C}^{\text{annealed}} = -\frac{1}{a\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \log \langle Z(J_0, J_1, \dots, J_{N-1}) \rangle \quad (14)$$

where the average $\langle \cdot \rangle$ has to be taken with respect to the coupling distribution.

To simplify our notation, a will be taken equal to 1. Physically a represents the mean area occupied by a molecule. Consequently, when writing $\beta\gamma$, we will in fact mean $\beta a\gamma$ for dimensional reasons.

Let us now present our results, the proofs of which can be found in the Appendix.

2.2 The results

Let us first introduce the family of probability distributions defined by the Boltzmann factor

$$d\mu(h_0, h_1, \dots, h_N; J_0, J_1, \dots, J_{N-1}) = \frac{1}{Z} e^{-\beta \sum_{i=0}^{N-1} J_i (1+|h_{i+1}-h_i|)} \delta(h_0) \delta(h_N) \quad (15)$$

where Z is the thermal normalization factor which can be expressed as

$$Z(J_0, J_1, \dots, J_{N-1}) = \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N e^{-\beta \sum_{i=0}^{N-1} J_i (1+|h_{i+1}-h_i|)} \delta(h_0) \delta(h_N), \quad (16)$$

Using quenched disorder to compute the free energy, we obtain the following equation to express the surface tension of the mixture like a convex combination of the pure component surface tensions

$$\begin{aligned}\gamma_{AB/C}^{quenched} &= -\frac{1}{\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \langle \log Z(J_0, J_1, \dots, J_{N-1}) \rangle \\ &= c \cdot \gamma_{A/C} + (1 - c) \cdot \gamma_{B/C},\end{aligned}\tag{17}$$

where $\gamma_{A/C}$ and $\gamma_{B/C}$ are the interfacial tensions for the A/C and B/C interfaces and where the average $\langle \cdot \rangle$ has to be taken with respect to the coupling distribution.

This kind of formula is therefore valid when the interface is quenched i.e. the system finds its equilibrium position within the configurations for a given set of couplings. Let us note that Eq.(17) is equivalent to Eq.(4).

The other approach, i.e. if we use the annealed disorder, leads to :

$$\begin{aligned}\beta \gamma_{AB/C}^{\text{annealed}} &= -\lim_{N \rightarrow \infty} \frac{1}{N} \log \langle Z(J_0, J_1, \dots, J_{N-1}) \rangle \\ &= -\log [c \cdot e^{-\beta \gamma_{A/C}} + (1 - c) \cdot e^{-\beta \gamma_{B/C}}]\end{aligned}\tag{18}$$

where $\gamma_{A/C}$ and $\gamma_{B/C}$ are the interfacial tension for the A/C and B/C interfaces and where the average $\langle \cdot \rangle$ has to be taken with respect to the coupling distribution. This is equivalent to Eq. (3).

Here, the variables J_i and h_i are treated on an equal basis. This implies that the molecules at the interface are sufficiently mobile to allow the interface to adjust itself, both in heights and in composition. This thus corresponds to a complete equilibrium case. Let us note that in this case there is no correlation between the different energetic costs J_i . A typical composition behaviour is given in Fig. 4 within the annealed approach. The mixtures

which follow this kind of behaviour are called perfect or ideal mixtures. More general formulae can be derived within this context for inclined interfaces due to the anisotropy of the SOS model [17].

INSERT HERE FIGURE 4

Finally, let us point out that more complex models for the heights h_i and for the couplings J_i could have been considered like gaussian distribution for instance but we can easily extend to these last case the previous results. The key ingredient has to be found in the application of the central limit theorem⁴.

3 The non-ideal case

Let us now consider the case of non perfect solutions, i.e. whenever the A molecule at the interface prefers to be in the neighborhood of another A molecule or a B molecule for instance.

In that case, after integrating over the h 's variables, cf Eq. (16), we will have asymptotically that

$$\langle Z \rangle \sim \int d\nu(J_0 \cdots J_{N-1}) \prod_i \left(\frac{2e^{-\beta(J_i+J_{i+1})/2}}{\beta\sqrt{J_i J_{i+1}}} \right) \quad (19)$$

where the random variables are no more independent and are distributed according to the probability measure $d\nu(J_0 \cdots J_{N-1})$. Let us consider as before that J_i may take two values J_A and J_B . For nearest neighbours couplings in the measure $d\nu$, the associated sum can then be written as

$$\langle Z \rangle = \frac{\sum_{J_0 \in \{J_A, J_B\}} \cdots \sum_{J_{N-1} \in \{J_A, J_B\}} \langle J_0 | T | J_1 \rangle \cdots \langle J_{N-2} | T | J_{N-1} \rangle}{\sum_{J_0 \in \{J_A, J_B\}} \cdots \sum_{J_{N-1} \in \{J_A, J_B\}} \langle J_0 | T' | J_1 \rangle \cdots \langle J_{N-2} | T' | J_{N-1} \rangle} \quad (20)$$

⁴cf Appendix

where the transfer matrices T and T' are given by

$$T = \begin{pmatrix} 2W_{AA} \frac{e^{-\beta J_A}}{\beta J_A} & 2W_{AB} \frac{e^{-\frac{1}{2}\beta(J_A+J_B)}}{\sqrt{\beta J_A \beta J_B}} \\ 2W_{AB} \frac{e^{-\frac{1}{2}\beta(J_A+J_B)}}{\sqrt{\beta J_A \beta J_B}} & 2W_{BB} \frac{e^{-\beta J_B}}{\beta J_B} \end{pmatrix} \quad (21)$$

$$T' = \begin{pmatrix} W_{AA} & W_{AB} \\ W_{AB} & W_{BB} \end{pmatrix} \quad (22)$$

where W_{AA} (resp. W_{AB}, W_{BB}) is the weight associated to the pair (J_i, J_{i+1}) which takes the value (J_A, J_A) (resp. (J_A, J_B) or (J_B, J_A) , (J_B, J_B)). In terms of interaction energies $\epsilon_{AA}, \epsilon_{BB}$ and ϵ_{AB} , we thus have

$$W_{AA} \sim e^{-\beta \epsilon_{AA}}$$

$$W_{BB} \sim e^{-\beta \epsilon_{BB}}$$

$$W_{AB} \sim e^{-\beta \epsilon_{AB}}$$

Therefore, we get with appropriate periodic boundary conditions

$$\lim_{N \rightarrow \infty} -\frac{1}{N} \log \langle Z \rangle = \lim_{N \rightarrow \infty} -\frac{1}{N} \log [Tr(T^N)/Tr(T'^N)] \quad (23)$$

where Tr denotes the trace of the matrix. This leads to

$$\beta \gamma_{AB/C}^{\text{annealed}} = -\log \lambda_{\max} + \log \lambda'_{\max} \quad (24)$$

where λ_{\max} (resp. λ'_{\max}) is the maximal eigenvalue of T (resp. T').

However, here, the concentration c is not fixed. To fix c , we have to consider the grand canonical approach by introducing the factor $e^{-\mu \frac{J_i+J_{i+1}}{2}}$ within the matrices of transfer T and T' . Taking into account that

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_i J_i = J_B + (J_A - J_B) \cdot c = -\frac{\partial}{\partial \mu} \log \lambda'_{\max} \quad (25)$$

we may inverse the relation $c(\mu)$ to get $\gamma_{AB/C}^{\text{annealed}}$ as a function of c .

This leads to

$$e^{-\beta\gamma_{AB/C}^{\text{annealed}}} = \alpha_1 e^{-\beta\gamma_{A/C}} + \alpha_2 e^{-\beta\gamma_{B/C}} + \Phi \quad (26)$$

where

$$\alpha_1 = \frac{z}{z + q + \sqrt{z^2 + q^2 + 2(2-q)z}} \quad (27)$$

$$\alpha_2 = \frac{q}{z + q + \sqrt{z^2 + q^2 + 2(2-q)z}} \quad (28)$$

and

$$\Phi = \frac{\sqrt{z^2 e^{-2\beta\gamma_{A/C}} + q^2 e^{-2\beta\gamma_{B/C}} + 2(2-q)z e^{-\beta\gamma_{A/C} - \beta\gamma_{B/C}}}}{z + q + \sqrt{z^2 + q^2 + 2(2-q)z}} \quad (29)$$

with

$$q = \frac{W_{AA}W_{BB}}{W_{AB}^2} \sim e^{2\beta(\epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2})} \quad (30)$$

The concentration c has to be found in z , namely :

$$z = \frac{(1-2c)^2 + 2c(1-c)q - (1-2c)\sqrt{(1-2c)^2 + 4qc(1-c)}}{2c(1-c)} \quad (31)$$

Limiting cases are easily recovered as

$c \rightarrow 0$:

$$e^{-\beta\gamma_{AB/C}} = e^{-\beta\gamma_{B/C}}$$

$c \rightarrow 1$:

$$e^{-\beta\gamma_{AB/C}} = e^{-\beta\gamma_{A/C}}$$

More general cases are presented in Fig. 5.

INSERT HERE FIGURE 5

These results are qualitatively in agreement with the experimental observations. Let us however stress that one gets a change of the concavity in the vicinity of $c = 0.5$. for the regime where q is small. This corresponds physically to the case where the system tries to have as many pairs of different molecules $A - B$ as possible or, in other words $\epsilon_{AB} \ll \frac{\epsilon_{AA} + \epsilon_{BB}}{2}$.

We thus have a different formula, Eq.(26), which can be compared to the Guggenheim's result. From the data for the mixture of acetone and diethylether extracted from [18], we get the results presented in Fig. 6. with a mean area occupied by a molecule $a = 30\text{\AA}^2$ and $\omega_{\text{Guggenheim}} = 450\text{cal/mole}$ and ours with $a = 30\text{\AA}^2$ and the associated $\omega \sim 750\text{cal/mole}$ ($q \sim e^{2\beta\omega}$, and q has the molecular interpretation introduced in (30)). As can be seen in this figure, both formulae lead to a good fit of the data with reasonable values of the parameters.

Moreover, it should be noticed that the two models also differ, from entropic reasons, since they refer to two different types of configuration.

INSERT HERE FIGURE 6

For the quenched $\gamma_{AB/C}$, we then have to calculate

$$\langle \log Z \rangle = \int d\nu(J_0 \cdots J_{N-1}) \sum_i (\beta J_i + \log \frac{2}{\beta J_i}) \quad (32)$$

In this case the configuration of couplings $(J_0, J_1, \dots, J_{N-1})$ is fixed. The summation in (32) is independent of the order of the J_i 's. We will always obtain cN values of J_A and $(1-c)N$ of J_B . The result is therefore equivalent to the ideal case

$$\gamma_{AB/C} = c \cdot \gamma_{A/C} + (1-c) \cdot \gamma_{B/C} \quad (33)$$

4 Concluding remarks

The introduction of the disorder within this problem of interfacial tension for binary mixtures has been helpful to understand the domain of validity of known formulae like (4) and (5). Indeed, within the Solid-On-Solid model, we have obtained for ideal systems that

$$e^{-\beta\gamma_{AB/C}^{\text{annealed}}} = c.e^{-\beta\gamma_{A/C}} + (1 - c).e^{-\beta\gamma_{B/C}} \quad (34)$$

and that

$$\gamma_{AB/C}^{\text{quenched}} = c.\gamma_{A/C} + (1 - c).\gamma_{B/C} \quad (35)$$

The formula for γ^{annealed} means that the molecules at the interface are sufficiently mobile to allow the interface to find its equilibrium configuration, both in heights and in composition. However, the formula for γ^{quenched} means that the molecules are not allowed to move at the interface, the only possible way to reach equilibrium is therefore to adjust the heights.

For non-ideal solutions, we have obtained an exact expression (26) which is qualitatively and quantitatively in good agreement with the observations. It complements Guggenheim's formulae for the case where the entropic contribution to the interfacial properties can become important such as for long chain molecules. A more detailed quantitative comparison with experimental data will be published elsewhere.

Let us also here remark that whenever the molecules A and B are distinguishable in size, the previous approach cannot be used any more since the heights h and the couplings J are no more independent random variables.

Moreover, we want to emphasize that these results can also be used to treat the equilibrium surface pressure of binary surfactant mixtures

Acknowledgements

J.R. wishes to thank the Centre de Recherche en Modélisation Moléculaire–
Université de Mons–Hainaut for kind hospitality and financial support.

A Appendix

A.1 Proof of the equation (17)

Applying the result of [17], we obtain

$$\beta\gamma_{A/C} = \beta J_{AC} - \log \frac{2}{\beta J_{AC}}. \quad (36)$$

Let us now consider the partition function

$$Z(J_0 \cdots J_{N-1}) = \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N e^{-\beta \sum_{i=0}^{N-1} J_i (1+|h_{i+1}-h_i|)} \delta(h_0) \delta(h_N). \quad (37)$$

Introducing the increments of heights

$$x_i = h_{i+1} - h_i, \quad (38)$$

we can show⁵ that the weak constraint $h_N = 0$ can be treated by some appropriate central limit theorem. We thus get asymptotically

$$Z(J_0, \dots, J_{N-1}) \sim \prod_i \int_{-\infty}^{+\infty} dx_i e^{-\beta J_i (1+|x_i|)} \quad (39)$$

Since

$$-\lim_{N \rightarrow \infty} \frac{1}{N} \langle \log Z(J_0 \cdots J_{N-1}) \rangle = -\lim_{N \rightarrow \infty} \frac{1}{N} \int_{-\infty}^{+\infty} \log Z. \prod_i P(J_i) dJ_i \quad (40)$$

where $P(J_i)$ represents the probability distributions of the random variables $\{J_i\}$, we get

$$\gamma_{AB/C}^{\text{quenched}} = -\frac{1}{\beta} \lim_{N \rightarrow \infty} \frac{1}{N} \sum \int_{-\infty}^{+\infty} \log \left(\frac{2e^{-\beta J_i}}{\beta J_i} \right) P(J_i) d(J_i) \quad (41)$$

$$= c \cdot \gamma_{A/C} + (1 - c) \cdot \gamma_{B/C} \quad (42)$$

■

⁵see section A.1.1

A.1.1 Proof of the equation (39)

We explain here the form of the equation (39). We apply for this a central limit theorem for which the random variables do not have identical probability distributions.

Let

$$Z(J_0, \dots, J_{N-1}) = \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N \exp[-\beta \sum_{i=0}^{N-1} J_i(1+|h_{i+1}-h_i|)] \delta(h_0) \delta(h_N) \quad (43)$$

We then have

$$\log Z(J_0, \dots, J_{N-1}) = \log \prod_i \int_{-\infty}^{+\infty} dx_i \exp^{-\beta J_i(1+|x_i|)} + \log f_{h_N}(0) \quad (44)$$

where

$$f_{h_N}(x) = \left\{ \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N \exp[-\beta \sum_{i=0}^{N-1} J_i(1+|h_{i+1}-h_i|)] \right. \quad (45)$$

$$\left. + z \sum_{i=0}^{N-1} (h_{i+1}-h_i) \delta(h_0) \delta(h_N-x) \right\} \quad (46)$$

$$\times \left\{ \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N \exp[-\beta \sum_{i=0}^{N-1} J_i(1+|h_{i+1}-h_i|)] \right. \quad (47)$$

$$\left. + z \sum_{i=0}^{N-1} (h_{i+1}-h_i) \delta(h_0) \right\}^{-1} \quad (48)$$

Let

$$h_N = \sum_{i=0}^{N-1} (h_{i+1}-h_i) = \sum_{i=0}^{N-1} X_i \quad (49)$$

where the X_i are independent random variables which are not identically distributed with distribution U_i . Now, we show that $\lim_{N \rightarrow \infty} \frac{1}{N} \log f_{h_N}(0) \rightarrow$

0 for $N \rightarrow \infty$. According to the probability measure

$$\begin{aligned} d\nu(x) &= [e^{-\beta J_i(1+|x|)}] / [\int_{-\infty}^{+\infty} dx e^{-\beta J_i(1+|x|)+zx}] \\ &= f_{h_N}(x) = \prod_i f_{X_i}(x) \end{aligned} \quad (50)$$

where z is chosen such that

$$\sum_{i=0}^{N-1} E(X_i) = 0 \quad (51)$$

Let U_i be the distributions of X_i and F_N the distribution of $\frac{\sum_i X_i}{s_N}$ where $s_N = \sum_i \sigma_i^2 (s_N \xrightarrow{N \rightarrow \infty} \infty)$. $F_N(x)$ is defined by a convolution

$$F_N(x) = U_1 * \dots * U_N(s_N x) \quad (52)$$

We denote by φ_{X_i} and φ_{h_N/s_N} the characteristic functions of U_i and F_N , respectively. Then

$$\phi_{h_N/s_N}(t) = \prod_i \varphi_{X_i}\left(\frac{t}{s_N}\right) \quad (53)$$

for any real t with the conditions that $E(X_i^3)$ exists and that $|\varphi|^\nu$ is integrable for some $\nu \geq 1$, we obtain as $N \rightarrow \infty$

$$f_N(x) - \mathcal{N}(x) - \frac{\mu_3^{(N-1)}}{6s_N^3}(x^3 - x)\mathcal{N}(x) = o\left(\frac{N}{s_N^3}\right) \quad (54)$$

where $\mathcal{N}(x)$ is the normal density and $\mu_3^{(N-1)} = \sum_{i=0}^{N-1} E(X_i^3)$ [19]. Thus we can apply this extended central limit theorem to obtain

$$h_N/s_N \xrightarrow{N \rightarrow \infty} \text{gaussian random variable.} \quad (55)$$

Since the density of h_N/s_N tends to the gaussian density and satisfies

$$f_{h_N/s_N}(x) = s_N f_{h_N}(s_N x) \quad (56)$$

one has

$$\log f_{h_N/s_N}(x) = \log[s_N f_{h_N}(s_N x)] \quad (57)$$

$$= \log s_N + \log f_{h_N}(s_N x) \quad (58)$$

Taking $x = 0$ and multiplying by $\frac{1}{N}$,

$$\frac{1}{N} \log f_{h_N/s_N}(0) = \frac{1}{N} \log s_N + \frac{1}{N} \log f_{h_N}(0) \quad (59)$$

we can conclude that, when $N \rightarrow \infty$

$$\frac{1}{N} \log f_{h_N}(0) \rightarrow 0 \quad (60)$$

This ends the proof. ■

A.2 Proof of the equation (18)

As in the subsection A.1, we have $Z(J_0 \cdots J_{N-1}) \sim \prod_i \int_{-\infty}^{+\infty} dx_i e^{-\beta J_i(1+|x_i|)}$ where x_i has been introduced in (38). Therefore,

$$- \lim_{N \rightarrow \infty} \frac{1}{N} \log \langle Z \rangle = - \lim_{N \rightarrow \infty} \frac{1}{N} \log \int_{-\infty}^{+\infty} Z(J_0, \cdots, J_{N-1}) \prod_i P(J_i) dJ_i \quad (61)$$

We get

$$\beta \gamma_{AB/C}^{\text{annealed}} = - \lim_{N \rightarrow \infty} \frac{1}{N} \sum_i \log \int_{-\infty}^{+\infty} \frac{2e^{-\beta J_i}}{\beta J_i} P(J_i) dJ_i \quad (62)$$

$$= - \log[c.e^{-\beta \gamma_{A/C}} + (1-c).e^{-\beta \gamma_{B/C}}] \quad (63)$$

■

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Figures captions

Figure 1: The considered binary mixture always in contact with C.

Figure 2: Fluctuating interface between the two media A and C.

Figure 3: The $d = 2$ Solid-On-Solid interface between the two media A and C.

Figure 4: The perfect solution case within the annealed approach.

Figure 5: The interfacial tension $\gamma_{AB/C}^{annealed}$ for a non-ideal binary mixture as a function of the concentration c , for $\beta\gamma_{AC} = 4 + \ln 2$, $\beta\gamma_{BC} = 1 - \ln 2$, and different values of the parameter q .

Figure 6: Comparison between experimental data of a Acetone-Diethylether mixture, our formula (26) for $q = 13.797$ and Guggenheim's formula (5) for $m = 0.25$ and $\omega = 450cal/mole$.

Figure 1

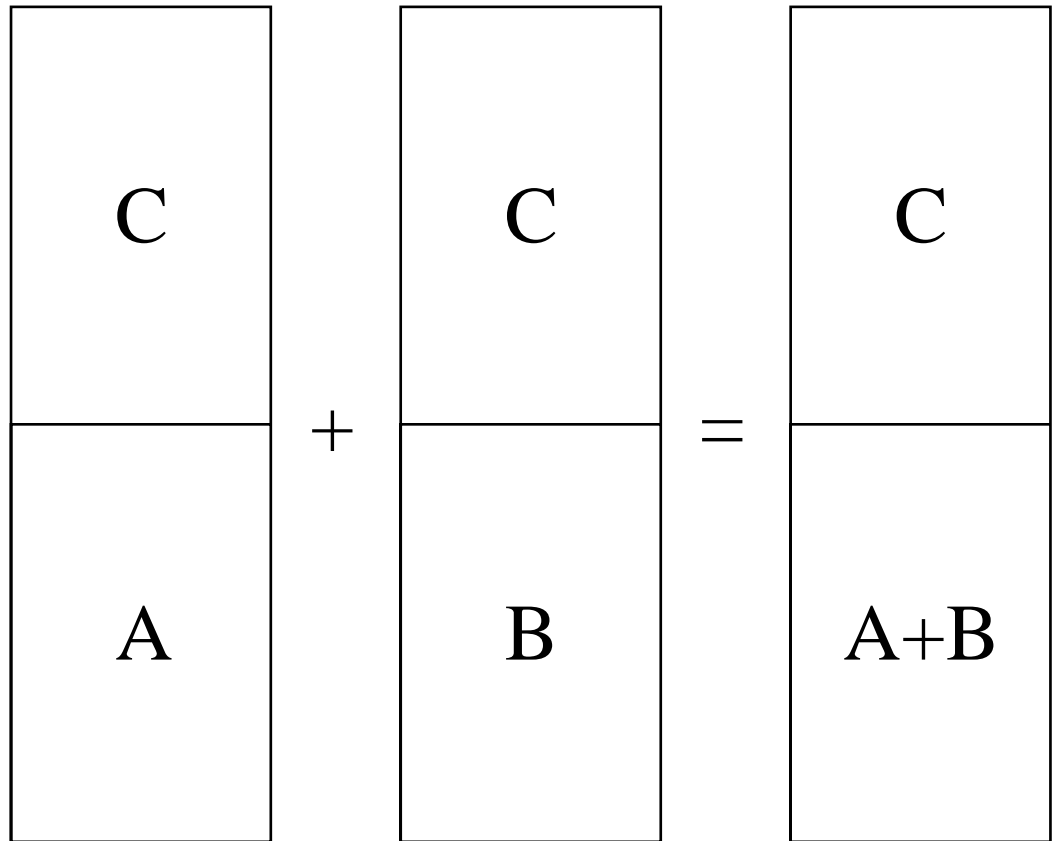


Figure 2

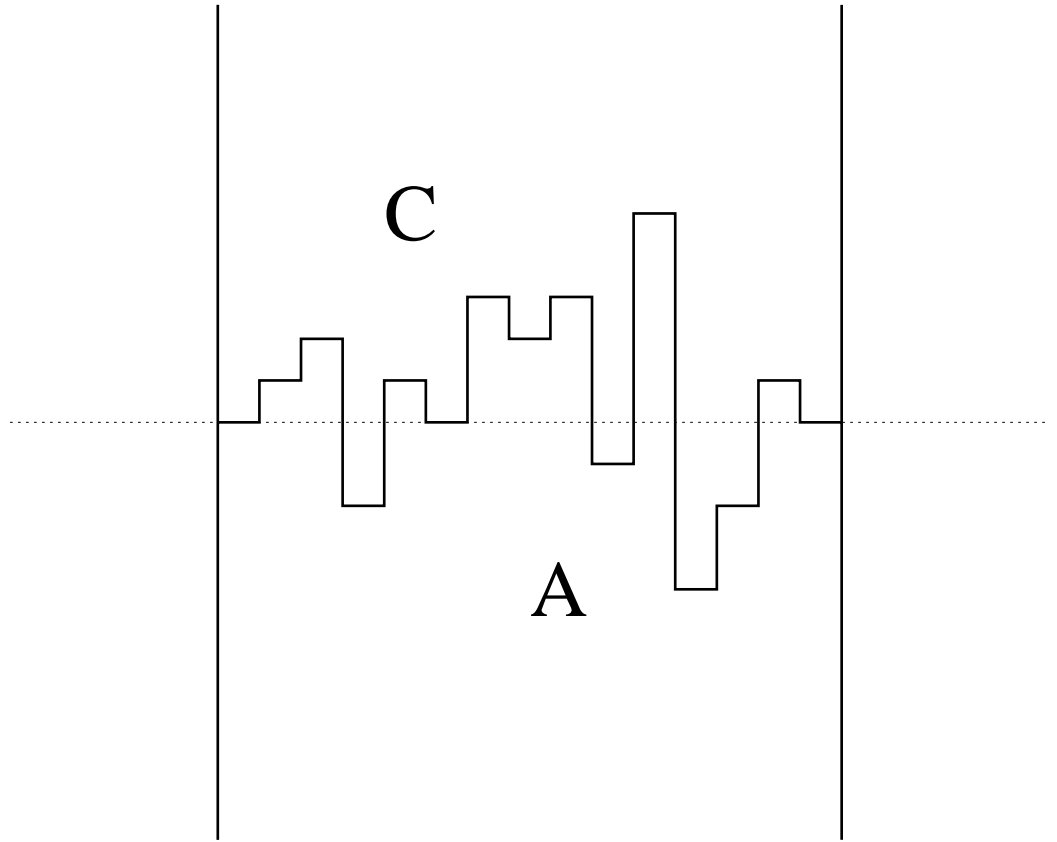


Figure 3

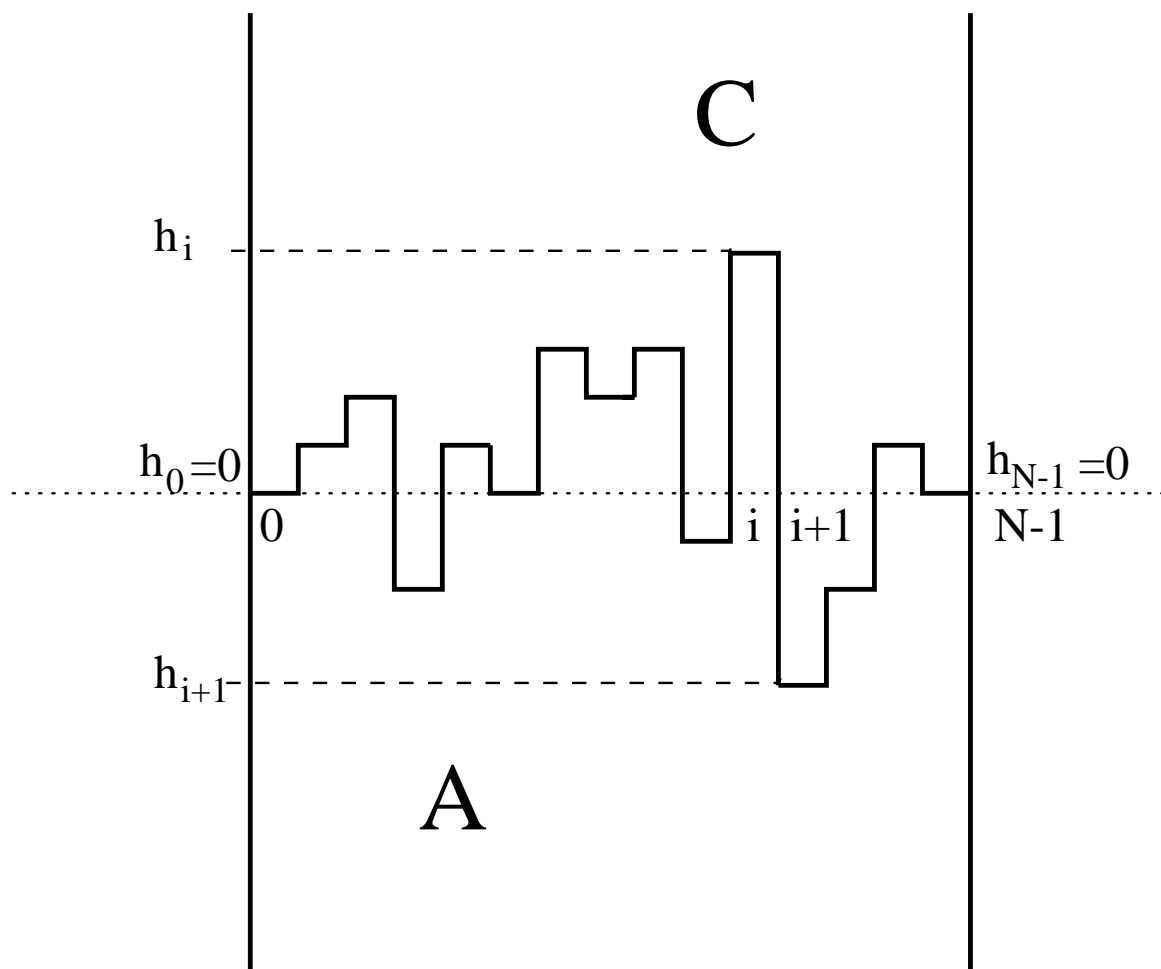


Figure 4

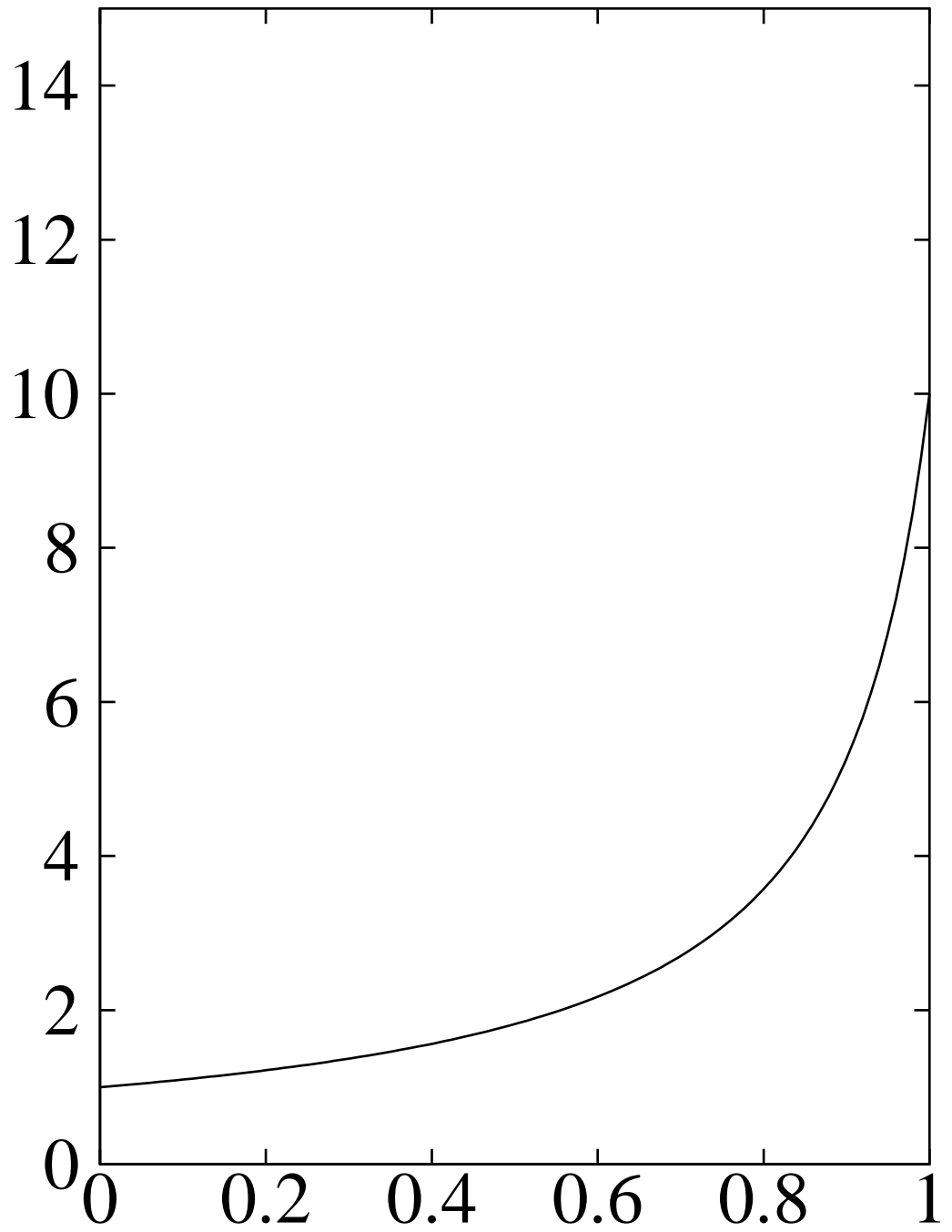


Figure 5

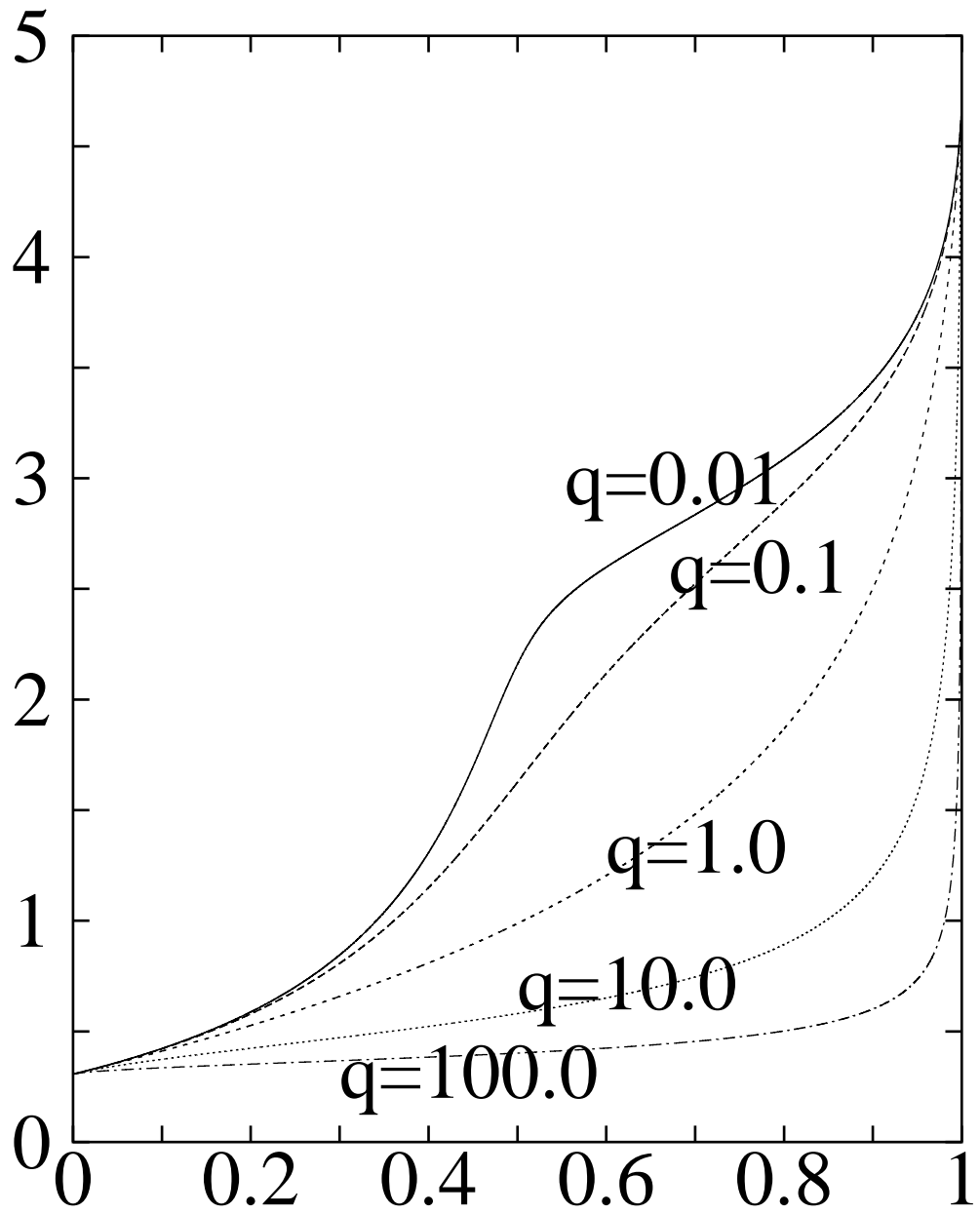


Figure 6

