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J. Phys. A: Math. Gen. 21 (1988) 3365-3377. Printed in the UK

Towards statistical mechanics of a 2D random cellular structure

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Received 7 July 1987, in final form 4 March 1988

Abstract. Using the methods of statistical mechanics we construct the partition function of a system of a large number of 2D cells that covers without pores or overlaps a flat surface. Each cell is defined by its position, area, perimeter and number of sides. Besides topological and space-filling constraints we impose new ones regarding the energy and maximum area of the cells. The entropy and free energy of the system are calculated and the mean values of the macroscopic parameters are determined in the equilibrium configuration. The results are compared with experimental ones for soap froths and metallurgical agreggates.

1. Introduction

Many systems in nature can be thought of as being made of cells that fill an available space. Examples are soap bubbles, metallurgical aggregates, undifferentiated biological tissues, etc. These are examples in three dimensions, but each of them can have a two-dimensional representation: soap bubbles can be constructed to simulate 2D froths [1-4]; the observed micrographic section of a polycrystalline metal is two dimensional and biological tissues can form 2D systems.

In spite of evident differences between these systems, they present common features: they divide a given portion of Euclidean space (2D or 3D) in cells and the coordination number, i.e. the number of edges that meet at the same vertex, is always three in 2D or four in 3D [1, 5]. Also some structures, such as biological tissues, soap bubbles and metallurgical aggregates in a sintering process, evolve in time but the evolution is so slow that we can consider the system stable over relatively long periods of time (minutes or hours).

The evolution of 2D systems in time can be determined by the parameter μ_2, the second moment of the distribution of n, the number of neighbours of the cells, and by the variation of the average area or perimeter of the cells [5, 6]. Aboav [7] showed that, in the case of a 2D soap froth, the apparent stabilisation found by Smith [8] in his experiment is premature. It is not clear that a soap froth attains a final stable configuration. On the other hand, the sintering process seems to reach a stable state [1, 5]. Probably metallurgical grains are also in a metastable configuration, but the evolution takes place at a very slow pace or it is stopped by defects and impurities [9]. The differences presented by those systems belong to their dynamics.

Within von Neumann's model [10] the variation of area of a given cell is proportional to the amount of gas that diffuses through its walls, i.e. it is proportional to the product of wall length (in 2D) and pressure difference (which is proportional to the curvature of the sides). Von Neumann concluded that (i) the rate of growth of each n-sided

bubble is the same at every time and (ii) the rate of growth of n-sided bubbles is proportional to the number of sides minus six.

Glazier *et al* [4], in a recent work, studied 2D soap froths and found that bubbles with the same number of sides can evolve at different rates, but on the average the evolution of n-sided bubbles follows von Neumann's results, namely, the average rate of growth of n-sided cells is proportional to $(n-6)$. They have also found that the mean value of the area of n-sided cells, $\langle a_n \rangle$, does not follow Lewis's law, which states that $\langle a_n \rangle$ depends linearly on n. Marder [11] developed a simple theory to explain the evolution of $\langle a_n \rangle$ in time.

The equilibrium configuration of 2D cellular systems has been studied by Rivier [1, 12-14] by applying the maximum entropy principle [15] and considering the geometrical and topological conditions as constraints on a generalised entropy. A relation between the variables is introduced in order to further maximise the entropy. The probability $f(n, a)$ of finding a cell of n sides and area a is calculated. The perimeter of the cells is also considered in one of the papers [13].

Following these ideas, we introduce here the energy of the cells as a constraint and take into account the fact that, for a given perimeter p, the maximum possible area of a cell is that of a regular polygon.

A method is presented that enables us to take into account the energy terms that arise from perimeter, area and/or number of sides, as well as the geometric, non-holonomic constraint quoted in the previous paragraph. Different assumptions about the energy terms will lead to particular evolution conditions of the configurations of the system.

Here we will assume the energy is proportional to the area and to the perimeter of the cells. The results show the utility of the method, give an insight on the nature of the problem and provide a basis for the choice of more appropriate sets of constraints to be imposed upon the system of interest.

2. The theoretical model

In order to apply the methods of statistical mechanics to cellular systems one must specify (i) the phase space and (ii) how to obtain the density function, i.e. the probability of finding the system in a given point of the phase space.

We consider an array of a large number of two-dimensional cells which cover without overlaps or pores a flat surface of area A and are characterised by their position, area, perimeter and number of sides (equal to the number of neighbouring cells) [1, 5].

Each configuration of this cellular system is associated with a point in a generalised phase space of coordinates $n_1, n_2, \ldots, n_N; p_1, p_2, \ldots, p_N; a_1, a_2, \ldots, a_N; \boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N$; n_i, p_i, a_i and $\boldsymbol{x}_i$ being the number of sides, perimeter, area and centre of mass coordinates of the i cell, and the density function is defined as

$$\rho(n^N, p^N, a^N, \boldsymbol{x}^N) = p(n_1, \ldots, n_N; p_1, \ldots, \rho_N; a_1, \ldots, a_n; \boldsymbol{x}_1, \ldots, \boldsymbol{x}_N). \tag{1}$$

The maximum entropy principle [15], as discussed in [13], will be utilised as a tool to derive the statistical mechanics of the problem. The aim of the method is to obtain the configuration of maximum entropy of the system consistent with the set of constraints. It associates different Lagrange multipliers to each constraint. As area and perimeter are linked through a non-holonomic relation, this assumption may be

redundant here. In fact, we will see in § 3 that the Lagrange multipliers associated with perimeter and area are not independent.

Also, one should be aware that we are applying a statistical mechanics technique to a system that has a large number of cells, but each element is a macroscopic entity, and not a microscopic one. Each cell is not characterised by, for example, position and momentum, as in a gas of particles, but by macroscopic parameters such as the number of sides, perimeter, area and position. The total number of cells, N, is also a variable of the problem. So, we are working in a kind of grand canonical ensemble that we call the super ensemble.

2.1. *The constraints*

A geometrical, non-holonomic constraint relates the area and perimeter of each cell. For a given perimeter p_i, and number of sides n_i, there is a maximum possible area $a^i_{\max}$ that is the area of the regular polygon of n_i sides:

$$a^i_{\max} = \frac{p_i^2 \operatorname{cotan}(\pi/n_i)}{4n_i}. \tag{2}$$

Before discussing the other constraints we define a sum operator over the phase space volume:

$$\Xi = \sum_{N=0}^{\infty} \prod_{j=1}^{N} \sum_{n_j=3}^{\infty} \int_0^{\infty} \mathrm{d}p_j \int_0^{a^j_{\max}} \mathrm{d}a_j \int_A \mathrm{d}\boldsymbol{x}_j. \tag{3}$$

Now, the normalisation condition is

$$\Xi\, \rho(n^N, p^N, a^N, \boldsymbol{x}^N) = 1 \tag{4}$$

the full filling of the area is

$$\Xi \sum_{j=1}^{N} a_j \rho(n^N, p^N, a^N, \boldsymbol{x}^N) = A \tag{5}$$

and the mean number of cells is

$$\Xi\, N\rho(n^N, p^N, a^N, \boldsymbol{x}^N) = \langle N \rangle. \tag{6}$$

Also, we must take into account the topological constraint given by the Euler condition to fill a 2D flat space: the average number of sides must be six [5, 13] (for a coordination number $Z = 3$). Then

$$\Xi \sum_{j=1}^{N} n_j \rho(n^N, p^N, a^N, \boldsymbol{x}^N) = 6\langle N \rangle. \tag{7}$$

The mathematical expression of the geometrical constraints is given by (4)-(7). The total energy of the system is introduced as an additional condition. We consider two terms of energy: the internal energy of the cells and the tension between them. Within a very simple model, the energy of interaction between the cells is taken as proportional to the length of contact [1, 13], i.e.

$$E_p = \tfrac{1}{2}\sigma \sum_{j=1}^{N} p_j \tag{8}$$

where σ is a linear energy coefficient, and the factor $\frac{1}{2}$ is introduced in order not to count the energy twice.

The internal energy is considered as proportional to the size (area) of the cell, and to the temperature (energy) of the gas (matter) inside it. Then if the system is assumed to be in equilibrium with a thermal bath, we have

$$E_i = \Omega(T) \sum_{j=1}^{N} a_j = \Omega(T)A \tag{9}$$

$\Omega(T)$ being the thermal energy per unit area, an increasing function of temperature. The total energy is

$$E = E_p + E_i. \tag{10}$$

Equations (9) and (10) yield to the last constraint:

$$\Xi \sum_{j=1}^{N} (\tfrac{1}{2}\sigma p_j + \Omega(T)a_j)\rho(n^N, p^N, a^N, x^N) = \langle E \rangle. \tag{11}$$

2.2. *The generalised entropy*

The density function $\rho(n^N, p^N, a^N, x^N)$, hereafter called ρ, may be determined within the maximum entropy formalism [12, 13, 15] by defining a generalised entropy:

$$\Psi = S - \alpha_1 \Xi\, \rho - \alpha_2 \Xi\, \rho \sum_{j=1}^{N} (\tfrac{1}{2}\sigma p_j + \Omega a_j)$$
$$- \alpha_3 \Xi\, \rho \sum_{j=1}^{N} a_j - \alpha_4 \Xi\, \rho \sum_{j=1}^{N} n_j - \alpha_5 \Xi\, \rho N \tag{12}$$

where the α_i are Lagrange multipliers and S is

$$S = -k_B \Xi\, \rho \ln(C^N \rho N!) \tag{13}$$

where k_B is the Boltzmann constant, C a dimensional factor and $N!$ is introduced to count correctly the number of states (i.e. to avoid the Gibbs paradox).

The maximum value of Ψ defines the state of statistical equilibrium. Soap froths and other cellular systems can be considered in equilibrium because they are invariant under elementary topological transformations (Aboav-Weaire law [5]); then, as discussed in [13], they are 'very near, or at, a fixed point under structural transformations'.

Within these considerations, the equilibrium density function is obtained by extremising Ψ and it gives

$$\rho = (C^N N! Z)^{-1} \exp\left(-\sum_{j=1}^{N} [\tfrac{1}{2}x_2 \sigma p_j + (x_2\Omega + x_3)a_j + x_4 n_j] - x_5 N \right) \tag{14}$$

where

$$x_i = \alpha_i / k_B \tag{15}$$

and

$$Z = \exp(1 + x_1)$$
$$= (C^N N!)^{-1} \exp\left(-\sum_{j=1}^{N} [\tfrac{1}{2}x_2 \sigma p_j + (x_2\Omega + x_3)a_j + x_4 n_j] - x_5 N \right) \tag{16}$$

is the partition function.

Now the normalisation condition (4) is included in Z and (5)-(7) and (11) may be written as

$$-\frac{1}{Z}\frac{\partial Z}{\partial x_2}=\langle E\rangle \tag{17a}$$

$$-\frac{1}{Z}\frac{\partial Z}{\partial x_3}=A \tag{17b}$$

$$-\frac{1}{Z}\frac{\partial Z}{\partial x_4}=6\langle N\rangle \tag{17c}$$

$$-\frac{1}{Z}\frac{\partial Z}{\partial x_5}=\langle N\rangle. \tag{17d}$$

Then, from the knowledge of the partition function Z and the values of the area A and energy $\langle E\rangle$ of the system, we can determine the four unknown Lagrange multipliers.

3. Determination of the partition function and the Lagrange multipliers

After a straightforward calculation, the partition function, defined in (16), is

$$Z=\exp\left(\frac{\exp(-x_5)AQ}{C}\right) \tag{18}$$

where Q is defined as

$$Q=\sum_{n=3}^{\infty}\exp(-x_4 n)\int_0^{\infty}\mathrm{d}p\,\exp(-\tfrac{1}{2}x_2\sigma p)\int_0^{p^2K_n}\mathrm{d}a\,\exp[-(x_2\Omega+x_3)a] \tag{19}$$

and

$$K_n=\frac{\operatorname{cotan}(\pi/n)}{4n}. \tag{20}$$

The constraint equations (17*a*,*b*,*c*,*d*) can be written as

$$-\exp(-x_5)\frac{A}{C}\frac{\partial Q}{\partial x_2}=\langle E\rangle=\varepsilon\langle N\rangle \tag{21a}$$

$$-\exp(-x_5)\frac{A}{C}\frac{\partial Q}{\partial x_3}=A=\eta\langle N\rangle \tag{21b}$$

$$-\exp(-x_5)\frac{A}{C}\frac{\partial Q}{\partial x_4}=6\langle N\rangle \tag{21c}$$

$$\exp(-x_5)\frac{A}{C}Q=\langle N\rangle \tag{21d}$$

where ε is the average energy and η the average area per cell.

Now, from (19), (21*a*) and (21*b*), one obtains

$$x_3=-x_2\Omega. \tag{22}$$

This implies, as should be suspected from the expression of the constraints, that the system is overconstrained: the average size of the cells is already restricted by energy (x_2) and geometry (x_4) considerations. The constraint over the perimeter acts also over the area because of the non-holonomic constraint relating the maximum value of the area of a cell with n, the number of sides, and p, the perimeter (2).

We define now the average perimeter energy per cell as

$$\varepsilon_{\mathrm{p}} = \Xi\, \rho \sum_{j=1}^{N} \tfrac{1}{2}\sigma p_j (\Xi\, \rho N)^{-1} = \varepsilon - \Omega\eta \tag{23}$$

and rewrite the constraint equation (21a) as

$$-\frac{1}{Q}\frac{\partial Q}{\partial x_2}\bigg|_{x_3=-x_2\Omega} = \varepsilon_p + \Omega\eta. \tag{21a'}$$

After some calculations, equations (21a') and (21b) yield

$$x_2 = 3\varepsilon_{\mathrm{p}}^{-1} \tag{24}$$

and (21c) becomes

$$\sum_{n=3}^{\infty} \exp(-x_4 n) K_n n = 6 \sum_{n=3}^{\infty} \exp(-x_4 n) K_n \tag{25}$$

which can be numerically solved and gives

$$x_4 = 0.326\,15. \tag{26}$$

We can now calculate the value of η, solving (21b) and using (24):

$$\eta = \frac{8\varepsilon_{\mathrm{p}}^2 \Phi_2}{3\sigma^2 \Phi_1} \tag{27}$$

where

$$\Phi_k = \sum_{n=3}^{\infty} \exp(-x_4 n) K_n^k. \tag{28}$$

The Φ_k are well defined quantities since x_4 is a known value given by (26).

Using (21b), (21d) and (27) we have

$$\exp(-x_5) = \frac{81\sigma^5 C}{128\varepsilon_{\mathrm{p}}^5 \Phi_2} \tag{29}$$

and

$$\langle N \rangle = \frac{3\sigma^2 \Phi_1 A}{8\varepsilon_{\mathrm{p}}^2 \Phi_2}. \tag{30}$$

As is to be expected, the mean number of cells is inversely proportional to the square of the energy per cell (as ε_{p} goes as the perimeter, $\langle N \rangle$ goes as (area per cell)$^{-1}$). Equation (29), together with (21b), yields

$$\varepsilon_{\mathrm{p}} = \frac{3\sigma^2 \Phi_1 A}{8\Phi_2(\langle E \rangle - \Omega A)}. \tag{31}$$

The problem is now formally solved. The partition function is

$$Z = \exp\left(\frac{3\sigma^2 \Phi_1 A}{8\varepsilon_{\mathrm{p}}^2 \Phi_2}\right) \tag{32}$$

and the distribution function is

$$\rho = \frac{1}{N!}\left(\frac{81\sigma^5}{128\varepsilon_p^5\Phi_1}\right)^N \exp\left(-\frac{3\sigma^2\Phi_1 A}{8\varepsilon_p^2\Phi_2} - \frac{3\sigma}{2\varepsilon_p}\sum_{j=1}^{N} p_j - x_4\sum_{j=1}^{N} n_j\right). \tag{33}$$

4. The entropy and the free energy

The entropy is obtained by substituting (33) in (14) and using the constraint equations (21):

$$S = k_B\left[4 + 6x_4 - \ln\left(\frac{81\sigma^5 C}{128\Phi_2\varepsilon_p^5}\right)\right]\frac{3\sigma^2\Phi_1 A}{8\varepsilon_p^2\Phi_2}. \tag{34}$$

The dimensional constant C^N is the volume in the generalised phase space of a state represented by the point (n^N, p^N, a^N, x^N). As C has dimensions of (length)^5 we define λ such that

$$C = \lambda^5 \tag{35}$$

where λ has dimensions of length and is the analogue of Planck's constant h in quantum statistical mechanics. We have, then, a lowest possible value for η. Equation (34) has a physical meaning for

$$\eta > \lambda^2 \tag{36}$$

which, through (26) and the numerical values of Φ_1 and Φ_2, implies that

$$\varepsilon_p \geqslant 4.8\sigma\lambda/2. \tag{37}$$

For values of $\varepsilon_p > 4.8\sigma\lambda/2$ or $\eta > \lambda^2$ the entropy is always positive and behaves as shown in figure 1. (Below these limits S goes through a maximum and then decreases.)

The total energy of the system is

$$E = \varepsilon\langle N\rangle = \frac{3\sigma^2\Phi_1 A}{8\Phi_2\varepsilon_p} + \Omega(T)A. \tag{38}$$

There are two terms of energy. The energy of interaction between cells, which is concentrated in the perimeters, decreases when one has few big cells in the system, i.e. it is inversely proportional to ε_p. When the cells are small, ε_p has a low value but the total perimeter (and the total energy) increases. The second term of (38) corresponds to the internal energy, which is constant for a fixed temperature.

If we consider an adiabatic equilibrium evolution ($\langle E\rangle$ constant), higher values of ε_p (the cells grow up) will increase the temperature of the system, transforming interaction energy into internal energy.

On the other hand, the current experimental situation is the isothermal one. Experimental results show that the size of the cells increases in time [2-4, 7]. In that case, the second term in (38) is constant and the total energy decreases. A final state of equilibrium should be attained when the free energy is a minimum.

The free energy is

$$F = E - TS. \tag{39}$$

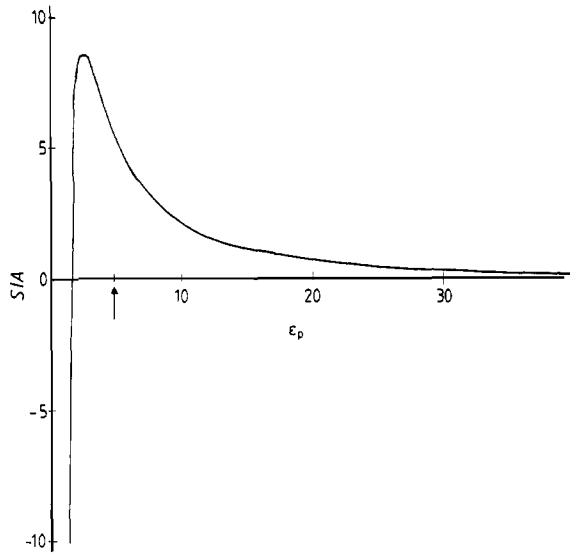

Figure 1. Plot of the entropy per unit area, S/A, as a function of the mean perimeter energy, ε_p. The units of S/A and ε_p are respectively k_B/λ^2 and $\sigma\lambda/2$. The arrow indicates the lower limit of ε_p as discussed in the text.

We are interested in the dependence of F on ε_p, for a fixed temperature. Then we write

$$F=\frac{3\sigma^2\Phi_1 A}{8\varepsilon_p\Phi_2}-k_B T\left[4+6x_4-\ln\left(\frac{81\sigma^5\lambda^5}{128\Phi_2\varepsilon_p^5}\right)\right]\frac{3\sigma^2\Phi_1 A}{8\varepsilon_p^2\Phi_2}. \tag{40}$$

A plot of F/A as a function of ε_p is shown in figure 2.

If the temperature is low, i.e. $T\leqslant\sigma\lambda/2k_B$, the free energy is monotonically decreasing in ε_p, implying that, if ε_p is allowed to vary, the system will evolve towards higher values of ε_p or η, without a final stable configuration. This is the case of macroscopic cellular systems.

If the temperature is high, i.e. $T\geqslant\sigma\lambda/2k_B$, the free energy presents a maximum†. In this case the final configuration will depend on the initial conditions. For a low initial value of ε_p, i.e. in the region to the left of the maximum of the free energy, the cells tend to shrink. For a high value of ε_p, in the region to the right of the maximum of F, the system evolution is such that the cells, on average, always grow up.

The characteristic temperatures are different for different systems because of the values of σ and λ. For a soap froth and other macroscopic cellular systems it is reasonable to look at the low-temperature free energy as the interface energy is much higher than $k_B T$.

Also, as is to be expected, the free energy is entropy dominated at high temperatures ($T=1.5$) and also for low values of ε_p, because in that case one has a high number of cells and thus a high entropy. Both energy and entropy tend to reduce the free energy when $\varepsilon_p\to\infty$, i.e. when the cells grow up, in agreement with the experimental results. However, in that limit one has a small number of cells, N, in the system and statistical arguments may no longer be valid.

† The free energy also exhibits a minimum for values of $\varepsilon_p<4.8\sigma\lambda/2$, i.e. in the region of negative entropy. This is a region without physical meaning.

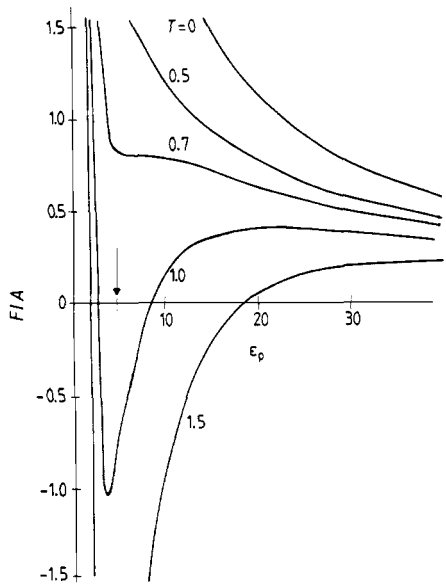

Figure 2. Plot of the free energy per unit area, F/A, as a function of the mean perimeter energy, ε_p. The units of F/A, ε_p and T are respectively $\sigma/2\lambda$, $\sigma\lambda/2$ and $\sigma\lambda/2k_B$. The arrow indicates the lower limit of ε_p as discussed in the text.

Although the system does not have a stable configuration, in terms of a minimum of the free energy, the evolution is very slow when compared with the characteristic times required to attain the statistical equilibrium, as was discussed in § 2. We assume it goes in a 'quasistatic' way through a succession of states of statistical equilibrium, for which the thermodynamical variables and the statistical distribution are well defined.

Also, one expects that if the system is isolated it will exhibit a different behaviour. It should be interesting to examine the evolution, if any, of a froth under adiabatic conditions.

5. Determination of the mean values and distributions of area, energy and number of sides

From the knowledge of the density function one can determine the relative number of cells with a particular area, energy (perimeter) and number of sides. These results together with the entropy and free energy, already discussed, provide a complete view of a given state of the system.

5.1. Average area

We are interested in two values: the average area per cell, η, given by (27), and the average area of an n-sided cell, that can be calculated *ab initio* from

$$\langle a_n \rangle = \Xi\, \rho \sum_{j=1}^{N} \delta_{n_j n} a_j \left(\Xi\, \rho \sum_{j=1}^{N} \delta_{n_j n} \right)^{-1} \tag{41}$$

where the numerator is the sum of the areas of all n-sided cells and the denominator is the number of n-sided cells. Using (33) one obtains

$$\langle a_n \rangle = \frac{8\varepsilon_p^2 K_n}{3\sigma^2}. \tag{42}$$

A plot of $\langle a_n \rangle$ as a function of n is shown in figure 3. The dependence of $\langle a_n \rangle$ on n is the same as the one of regular polygons with different numbers of sides but equal perimeters (compare (42) and (20) with (2)). It implies that the sides of low-n cells must be longer, on the average, than those of high-n cells. This is unreasonable if cells with different numbers of sides are going to fit without pores or overlaps. A restriction on the mean value of the side lengths should be imposed to improve the model. We will return to this point in § 6.

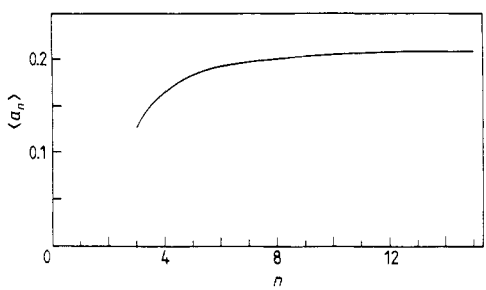

Figure 3. Plot of the average area of the n-sided cells, in units of ε_p^2/σ^2, as a function of the number of sides, n. It exhibits the same dependence on n as the area of regular polygons with equal perimeters.

5.2. Average energy

The average total energy and perimeter energy are given by ε and ε_p respectively. One is also interested in the mean energy of n-sided cells:

$$\varepsilon_p(n) = \Xi\, \rho \sum_{j=1}^{N} \tfrac{1}{2}\sigma p_j \delta_{n_j n} \left(\Xi\, \rho \sum_{j=1}^{N} \delta_{n_j n} \right)^{-1} \tag{43}$$

and

$$\varepsilon(n) = \varepsilon_p(n) + \Omega \langle a_n \rangle. \tag{44}$$

We obtain that $\varepsilon_p(n)$ is independent of n:

$$\varepsilon_p(n) = \varepsilon_p \tag{45}$$

which is coherent with the results obtained for $\langle a_n \rangle$: the mean perimeter of the cells is independent of n. But this is not in agreement with experiments and numerical simulations. A comment on this point is also presented in § 6.

5.3. Distribution of the number of sides

The relative number of n-sided cells, $w(n)$, can be calculated as

$$w(n) = \Xi\, \rho \sum_{j=1}^{\infty} \delta_{n_j n} \, (\Xi\, \rho N)^{-1}. \tag{46}$$

Using (33) we get

$$w(n) = \exp(-x_4 n) K_n \left(\sum_{n=3}^{\infty} \exp(-x_4 n) K_n \right)^{-1}. \tag{47}$$

This result differs from that of Rivier and Lissowski [12] because of the factor K_n.

A plot of $w(n)$ against n is shown in figure 4. One can see that $w(n)$ decreases when n increases and there is not a maximum for $n \approx 5$ or 6 as in the results of [2, 3, 7]. Nevertheless, when the froth evolves in time there is a shift of the maximum of the distribution to lower values of n [7]. This result could then be interpreted as the $t \to \infty$ configuration of the distribution in n. However, the evolution predicted by the model refers only to the average cell size (ε_p or η), the distribution $w(n)$ does not change with time, energy or temperature.

The second moment, μ_2, of the distribution in n was also calculated:

$$\mu_2 = \sum_{n=3}^{\infty} w(n)(n-6)^2 = \langle n^2 \rangle - 36 \tag{48}$$

or

$$\mu_2 = \sum_{n=3}^{\infty} \exp(-x_4 n) K_n n^2 \left(\sum_{n=3}^{\infty} \exp(-x_4 n) K_n \right)^{-1} - 36. \tag{49}$$

The numerical result is

$$\mu_2 = 10.16 \tag{50}$$

which is bigger than the experimental values. The evolution of the froths presented by Weaire and Kermode [2, 3], Glazier *et al* [4], Aboav [7] and Anderson *et al* [16] exhibits a value of μ_2 that increases with time. The high value obtained here for μ_2 is further evidence that this distribution in n could be regarded as a limiting one.

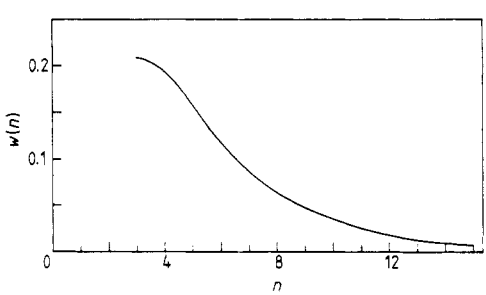

Figure 4. Plot of the relative number of n-sided cells, $w(n)$, as a function of n.

6. Discussion and conclusions

We have presented a formalism to study a random cellular structure in two dimensions taking into account geometrical and physical constraints. The constraints considered in the description of the method were

(i) the full filling of the space,

(ii) the Euler condition ($\langle n \rangle = 6$),

(iii) the interaction and bulk energy, and

(iv) a geometrical non-holonomic constraint relating the area, perimeter and number of sides.

But one can easily modify them or add other ones.

Within this simple model, it is possible to calculate the partition function and the thermodynamical variables.

We have obtained a distribution function of the number of sides, $w(n)$, that seems to correspond to the $t \to \infty$ configuration of a soap froth. However, the mean value of the energy of perimeter $\varepsilon_p(n)$ is independent of n. That means that the average length of the sides goes as n^{-1}. This is not geometrically sound if the cells must fit to cover the surface without pores or overlaps. One must then impose a new geometrical constraint on the perimeter, introducing a n-independent mean value for the side lengths (the simplest suitable relation between the side lengths and n). The average area of n-sided cells will also be affected by this new constraint.

We remark that the main difference between this calculation and that of Rivier *et al* [5, 12–14] is that we consider independent constraints. A relation between the perimeter and the number of sides is obtained in [13], assuming some constraints are not independent. We expect that taking a common mean value for the side lengths, one recovers those results. Calculations in this sense are now in progress.

On the other hand, the behaviour of the free energy as a function of ε_p appears to be in agreement with that of real systems. The free energy depends on the value of the temperature, compared with a critical value T_c:

(i) if $T < T_c$ the free energy is a monotonically decreasing function of ε_p and there is no final stable configuration;

(ii) if $T > T_c$ the free energy presents a maximum. If initially ε_p lies to the left of the maximum the evolution is such that ε_p will decrease. On the other hand, if the initial value of ε_p lies to the right of the maximum, the cells grow up and there is no final stable configuration (although $w(n)$ remains invariant).

The value of T_c is approximately given by $k_B T_c \approx \sigma\lambda/2$, where the values of σ and λ are typical of each system.

The model must be improved. Firstly one needs to take into account the energy related to the angle between the sides of the cell. A stable vertex has the three sides forming angles of 120° [1]. Any deviation should increase the energy. This term will introduce a dependence of the energy on the number of sides.

Also, as was mentioned before, a common average length of the sides must be imposed.

Calculations taking these two contributions into account are now in course. We expect a better agreement with experimental and numerical simulation results for soap froths and metallurgical aggregates.

Anyway, it is clear that, besides the geometrical constraints, energy considerations are relevant to a correct description of those systems and that the free energy has a qualitative behaviour which corresponds to the evolution in time of soap froths.

Acknowledgments

One of us (RMCA) acknowledges the kind hospitality of the Blackett Laboratory of Imperial College, London, during her stay and the British Council and CAPES (Brazil)

for financial support. We thank Professor Nicholas Rivier who suggested the idea of this work and acknowledge discussions with E Anda, M Foglio, E Dubois-Violette, R Jullien, P Pfeuty and J Friedel. This work was also supported by Brazilian agencies CNPq and FINEP.

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