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Beyond the Kolmogorov Johnson Mehl Avrami kinetics: inclusion of the spatial correlation

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Abstract. The Kolmogorov-Johnson-Mehl-Avrami model, which is a nucleation and growth Poissonian process in space, has been implemented by taking into account spatial correlation among nuclei. This is achieved through a detailed study of a system of distinguishable and correlated dots (nuclei). The probability that no dots be in a region of the space has been evaluated in terms of correlation functions. The central point of the paper is the application of the theory to describe nucleation and growth in two dimensions under constant nucleation rate, where correlation among nuclei depends upon the size of the nucleus. This is a typical case occurring in transformation governed by particle diffusion. We also propose a simple formula for describing the phase transition kinetics under this circumstance.

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1 Introduction

It is common knowledge that in order a process in space be Poissonian, dots must be dispersed at random throughout the whole space. Kolmogorov-Johnson-Mehl-Avrami [1–3] applied this process for describing phase transformations based on nucleation and growth of the new phase in the parent phase. In their model nuclei are preexisting and the nucleation rate law is given *a priori* and concerns all the nuclei. This means that nuclei already covered by the new phase can start growing; these nuclei were christened phantoms by Avrami. To the end of reaching a simple formula for the kinetics it is necessary to include in the computation the contribution of phantoms [4], although they apparently do not contribute to the new phase, and more than that if they did the model simply would fail. As a matter of fact there exists a class of functions that cannot be used for approximating the growth law; for instance one of these, usually employed in diffusional growths [5], is $r = t^{1/2}$, r being the linear dimension of nucleus. This limit of the KJMA model can be overcome by simply considering the actual nucleation, that is eliminating the phantom nuclei. Nevertheless this alternative point of view requires a more complex mathematical treatment; since the actual nucleation is limited to the untransformed space, correlation among nuclei must be taken into account [6]. Besides it is also possible that around a growing nucleus there be a zone where nucleation is strongly reduced, for example because of the stress induced by the new phase or because of a diffusional field. In a case like this the introduction of the correlation function would be compulsory, and as witnesses by the number of papers issued since 2000 [7–12], correlated nucleation in KJMA-type phase transitions has becoming an argument of great moment.

The aim of the present paper is to give a comprehensive and a quite general formulation of some results that we have already published [6,8,12]. Specifically the novelty are: i) the detailed demonstration of the exact kinetics of nucleation and growth in the case of non random and non simultaneous nucleation and, ii) using the result i), at the second order in the correlation functions, to evaluate the kinetics in case in which the island of radius $R(t)$ is surrounded by a capture zone of thickness $\rho = \text{const}$. The latter is the starting point for treating the kinetics by using the actual nucleation rate that is, in turn, accessible by experiment.

The paper is organized as follows: In Section 2, we describe the theory for treating a set of distinguishable classes of dots. In particular, the central point of the stochastic approach is to evaluate the probability, Q_0, that no dots occur into a region of a given volume. This is achieved by exploiting the relation [13] $Q_0 = \lim_{e^{ik}\to 0} \langle e^{ikN} \rangle$, where N is the stochastic variable number of dots and k is a parameter. The brackets stand for average over the distribution that will be introduced shortly. Furthermore,

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one can demonstrate that $\left\langle e^{ikN}\right\rangle = L\left[\{\exp(ik\chi)-1\}\right]$, in which L is an appropriate functional and χ is the characteristic function of the dot classes. The bulk of calculation is confined in the Appendices. Application of the theory to KJMA-type phase transitions is presented in Section 3 for correlation functions depending on nucleus size.

2 Stochastic theory of distinguishable dots

2.1 Definitions

Let us consider a countable set of distinguishable classes of dots. It goes without saying that within each class dots are indistinguishable. Moreover dots are correlated one another independently of the class they belong.

a) Following Van Kampen [13], each state of the sample space consists of:
   (i) a non negative integer m;
   (ii) a non negative integer s;
   (iii) a m-tupla of strictly positive integers $n_1, n_2, n_3, \cdots, n_m$, in such a way that their sum is equal to s. The m-tupla is a partition of the integer s.

   For each m, s and $(n_1, n_2, n_3, \cdots, n_m)$, s d-dimensional real variables exist each of them ranging the whole space:

$$\underbrace{\{\mathbf{x}_1,\cdots,\mathbf{x}_{n_1}\}_1,\{\mathbf{x}_1,\cdots,\mathbf{x}_{n_2}\}_2,\cdots,\{\mathbf{x}_1,\cdots,\mathbf{x}_{n_m}\}_m}_{s} \in \Re^{ds} \quad (1)$$

b) The probability distribution over these states is given by a sequence of nonnegative functions, Q, defined in the domain (1) and normalized according to

$$1 = Q^{(0)} + \sum_{\{1\}}\sum_{s}\sum_{\prod^s_{\{1\}}}\frac{1}{n_i!}\int Q^{(1)}_{\pi^s_i} d^s\mathbf{x} + \sum_{\{2\}}\sum_{s}\sum_{\prod^s_{\{2\}}}\frac{1}{n_i!n_j!}\int Q^{(2)}_{\pi^s_{ij}} d^s\mathbf{x} + \sum_{\{3\}}\sum_{s}\sum_{\prod^s_{\{3\}}}\frac{1}{n_i!n_j!n_k!}\int Q^{(3)}_{\pi^s_{ijk}} d^s\mathbf{x} + \cdots \quad (2)$$

$\{1\}$ indicates the set of all classes, $\{2\}$ the set of all distinct couples of classes, $\{3\}$ the set of all distinct terns and so on. With the adjective *distinct* we signify that, for example, the 3! possible terns made up by the classes ijk are a unique tern. s is the total number of dots, m is the number of classes and then $s \geq m$ is compulsory. $\Pi^s_{\{m\}}$ is the set of all partitions of s with m integers and, $\pi^s_{i_1,i_2\cdots i_m}$ is an element of $\Pi^s_{\{m\}}$. By the same token employed for classes, the set of all co-ordinates will be indicated by $\langle 1\rangle$, the set of all distinct couples of co-ordinates by $\langle 2\rangle$ and so on. Although we are using the same symbol as average, misunderstanding between the two is prevented by the context and by the fact that the sets of coordinates appears only as a sum index.

Let U be a function on the same state space as Q' s of the form $U = U^{(1)} + U^{(2)} + U^{(3)} + \cdots$, where $U^{(m)} = \sum^m_{\{1\}}\sum^s_{\langle 1\rangle} u_i(\mathbf{x}_\nu)$ and the subscript of u refers to the classes while that of $\mathbf{x}$ to co-ordinates, then its average over Q' s will be

$$\left\langle U\right\rangle = \left\langle U^{(1)}\right\rangle_{\{1\}} + \left\langle U^{(2)}\right\rangle_{\{2\}} + \left\langle U^{(3)}\right\rangle_{\{3\}} + \cdots \quad (3)$$

$$\left\langle U^k\right\rangle = \left\langle U^{(1)k}\right\rangle_{\{1\}} + \left\langle U^{(2)k}\right\rangle_{\{2\}} + \left\langle U^{(3)k}\right\rangle_{\{3\}} + \cdots \quad (4)$$

In the following we will compute $\langle U\rangle$, $\langle U^2\rangle$ and $\langle U^3\rangle$ and we will define the so-called f-functions and correlation functions (CFs) [13], nevertheless the bulk of calculation is reported in the appendices.

By using a short notation: $U^{(1)} = \sum_{\langle 1\rangle} u_i$, $U^{(2)} = \sum_{\langle 1\rangle} u_i + \sum_{\langle 1\rangle} u_j$. The superscript (1) stands for the presence of a single class ($m = 1$) which is specified by the subscript i of the single-variable function u_i, where the variable dependence is understood. By the same token the superscript (2) stands for the presence of two classes ($m = 2$), namely i, j.

2.2 Average quantities

The average of $U^{(1)}$reads

$$\left\langle U^{(1)}\right\rangle = \sum_{\{1\}}\sum_{s}\sum_{\prod^s_{\{1\}}}\frac{1}{n_i!}\int Q^{(1)}_{\pi^s_i}\sum_{\langle 1\rangle} u_i\, d^s\mathbf{x} = \sum_{\{1\}}\sum_{s}\sum_{\prod^s_{\{1\}}}\frac{n_i}{n_i!}\int u_i\, d\mathbf{x}\int Q^{(1)}_{\pi^s_i} d^{s-1}\mathbf{x} \quad (5)$$

which, defining the function $h_i \equiv \sum_s \sum_{\prod^s_{\{1\}}} \times \frac{n_i}{n_i!}\int Q^{(1)}_{\pi^s_i} d^{s-1}\mathbf{x}_i$, can be rewritten as

$$\langle U^{(1)}\rangle = \sum_{\{1\}}\int u_i\, h_i\, d\,\mathbf{x}_i \equiv \sum_{\{1\}}(u_i h_i). \quad (6)$$

By following a similar path of computation and defining the functions

$$h_{i,j} \equiv \sum_{s}\sum_{\prod^s_{\{2\}}}\frac{n_i}{n_i!n_j!}\int Q^{(2)}_{\pi^s_{ij}} d^{n_i-1}\mathbf{x}_i d^{n_j}\mathbf{x}_j \text{ and } h_{i,jk} \equiv \sum_{s}\sum_{\prod^s_{\{3\}}}\frac{n_i}{n_i!n_j!n_k!}\int Q^{(3)}_{\pi^s_{ijk}} d^{n_i-1}\mathbf{x}_i d^{n_j}\mathbf{x}_j d^{n_k}\mathbf{x}_k$$

one obtains

$$\langle U^{(2)}\rangle = \sum_{\{1\}}\sum_{\{1\}\backslash i}(u_i h_{i,j}) \quad (7)$$

$$\langle U^{(3)}\rangle = \sum_{\{1\}}\sum_{\{2\}\backslash i}(u_i h_{i,jk}) \quad (8)$$

where the symbol $\{m\}\backslash i$ means that all the m-tuplas are considered that do not contain the i-class and, as in equation (5), the parenthesis denote an integration. It is now possible to define the f-functions for any single class, that, at odds with those defined in [13], take into account the presence of the other classes, as

$$f_i \equiv h_i + \sum_{\{1\}\backslash i} h_{i,j} + \sum_{\{2\}\backslash i} h_{i,jk} + \sum_{\{3\}\backslash i} h_{i,jkl} + \cdots \quad (9)$$

and thus one ends up with

$$\langle U\rangle = \sum_{\{1\}} (u_i f_i). \quad (10)$$

The meaning of the f_i-function is immediate: the term $f_i d\mathbf{x}_i$ gives the probability of finding a dot (any) belonging to the i class in the volume element $d\mathbf{x}_i$ around $\mathbf{x}_i$, irrespective of the location of the other dots.

As far as the evaluation of $\langle U^2\rangle$ and $\langle U^3\rangle$ are concerned, the computation is more involved. However even in this case it is profitable to define f_{ij} and f_{ijk} functions for couples and terns of classes such that, $f_{ij}\, d\mathbf{x}_i\, d\mathbf{x}_j$ gives the probability of finding a dot of the i class in the element $d\mathbf{x}_i$ around $\mathbf{x}_i$ and a dot of the j class in the element $d\mathbf{x}_j$ around $\mathbf{x}_j$, irrespective of the location of the other dots; in a similar way f_{ijk} is defined. The evaluation of the averages, which have been reported in the Appendix A, leads to the results:

$$\langle U^2\rangle = \sum_{\{1\}} (u_i^2 f_i) + \sum_{\{1\}}\sum_{\{1\}} (u_i u_j f_{ij}) \quad (11)$$

$$\langle U^3\rangle = \sum_{\{1\}} (u_i^3 f_i) + 3\sum_{\{1\}}\sum_{\{1\}} (u_i^2 u_j f_{ij}) + \sum_{\{1\}}\sum_{\{1\}}\sum_{\{1\}} (u_i u_j u_k f_{ijk}). \quad (12)$$

2.3 The functional "L"

Let us now define the following functional of the stochastic variables $\{u\}$

$$L\big[\{u\}\big] \equiv \left\langle \prod_{\langle 1\rangle}^{n_i} (1+u_i) \prod_{\langle 1\rangle}^{n_j} (1+u_j) \prod_{\langle 1\rangle}^{n_k} (1+u_k)\cdots \right\rangle. \quad (13)$$

By making use of the averages of the previous section, equation (13) can be written as

$$\begin{aligned} L\big[\{u\}\big] =& 1 + \sum_{\{1\}}\sum_{s}\sum_{\prod_1^s} \frac{1}{s!}\left(u_1^s f_s\right) \\ &+ \sum_{\{2\}}\sum_{s}\sum_{\prod_2^s} \frac{1}{n_1! n_2!}\left(u_1^{n_1}\, u_2^{n_2}\, f_{n_1 n_2}\right) + \cdots \\ =& 1 + \sum_{m}\sum_{\{m\}}\sum_{s}\sum_{\prod_m^s} \frac{1}{n_1!\cdots n_m!} \\ &\times \left(u_1^{n_1}\cdots u_m^{n_m} f_{n_1\cdots n_m}\right) \end{aligned} \quad (14)$$

where $f_{n_1\cdots n_m}$ denotes the f-function that depends upon $s=\sum_{i=1}^m n_i$ variables of which n_1 of class 1, n_2 of class 2 and so on. The details of the computation are reported in Appendix C.

2.4 Correlation functions

We are now in a position to define the CFs, g_m, through the cluster expansion of the f-functions [13]. For the sake of clearness we report the case of four variables, two classes and the partition $(n_1, n_2) = (2, 2)$, as follows:

$$\begin{aligned} f_{2,2}(1,2,\bar{3},\bar{4}) =& g_1(1)g_1(2)g_1(\bar{3})g_1(\bar{4}) + g_2(1,2)g_2(\bar{3},\bar{4}) \\ &+ g_2(1,\bar{3})g_2(2,\bar{4}) + g_2(1,\bar{4})g_2(2,\bar{3}) \\ &+ g_1(1)g_3(2,\bar{3},\bar{4}) + g_1(2)g_3(1,\bar{3},\bar{4}) \\ &+ g_1(\bar{3})g_3(1,2,\bar{4}) + g_1(\bar{4})g_3(1,2,\bar{3}) \\ &+ g_1(1)g_1(2)g_2(\bar{3},\bar{4}) + g_1(1)g_1(\bar{3})g_2(2,\bar{4}) \\ &+ g_1(1)g_1(\bar{4})g_2(2,\bar{3}) + g_1(2)g_1(\bar{3})g_2(1,\bar{4}) \\ &+ g_1(2)g_1(\bar{4})g_2(1,\bar{3}) + g_1(\bar{3})g_1(\bar{4})g_2(1,2) \\ &+ g_4(1,2,\bar{3},\bar{4}), \end{aligned} \quad (15)$$

where the bar distinguishes the class. In order to obtain the expansion, in the first place, we need to determine the set, p_4, of the partition of 4, in which the generic element of the set is (k_1, k_2, k_3, k_4) and the positive integers k_i are determined according to the fulfillment of the relation $4 = 1k_1 + 2k_2 + 3k_3 + 4k_4$; in this case: (4,0,0,0), (0,2,0,0), (1,0,1,0), (2,1,0,0) and (0,0,0,1). The first element implies four functions of one variable, the second element two functions of two variables and so on, as in equation (15). The second step is to form, within each element of the set p_4, the set, P_4, of all the permutations which give an original (independent) contribution.

The generalization to the case of s variables, m classes and the partition $(n_1, \cdots, n_m)$ leads to

$$f_{n_1, n_2\cdots n_m} = \sum_{p_s}\sum_{P_s} \prod^{k_1} g_1 \cdots \prod^{k_n} g_n \cdots \prod^{k_s} g_s. \quad (16)$$

The short notation $\prod^{k_n} g_n$ indicates the product of k_n n-variable CFs. The n-variables are linked to the m classes, *i.e.* there are ν_1^n variables of class 1, ν_2^n variables of class 2 and so on, in such a way that

$$\sum_{j=1}^{m} \nu_j^n = n. \quad (17)$$

It can happen that some of the k_n m-tuples coincides (for example in Eq. (15) $g_2(1,\bar{3})$ and $g_2(2,\bar{4})$ contain the same m-tupla, *i.e.* the couple $\nu_1^2 = 1, \nu_2^2 = 1$), therefore, if $\mu(n/m)$ is the index that refers to the μth distinct m-tuple satisfying equation (17), and $k_{\mu(n/m)}$ is the multiplicity of $\mu(n/m)$, *i.e.* the number of times it occurs, equation (16) can be written as

$$f_{n_1, n_2\cdots n_m} = \sum_{p_s}\sum_{P_s}\prod_{n}\prod_{\mu(n/m)} \left[g_n(\nu_{1\mu}^n \cdots \nu_{m\mu}^n)\right]^{k_{\mu(n/m)}} \quad (18)$$

where

$$\sum_{\mu(n/m)} k_{\mu(n/m)} = k_n \tag{19}$$

and

$$\sum_n \sum_{\mu(n/m)} k_{\mu(n/m)} \nu^n_{j\mu} = n_j \tag{20}$$

and the notation $g_n(\nu^n_{1\mu} \cdots \nu^n_{m\mu})$ stands for $g_n(\mathbf{x}^{(1)}_1, \cdots, \mathbf{x}^{(1)}_{\nu^n_{1\mu}}, \mathbf{x}^{(2)}_1, \cdots, \mathbf{x}^{(2)}_{\nu^n_{2\mu}} \cdots, \mathbf{x}^{(m)}_1, \cdots, \mathbf{x}^{(m)}_{\nu^n_{m\mu}})$, where the superscript refers to the class.

The following step is to determine the number of distinct permutations. Terms are not different if they differ by the order of variables of the same class inside the individual g_n's or by the order of factor g_n whose m-tuple, $\nu^n_{1\mu} \cdots \nu^n_{m\mu}$, pertains to the same $\mu(n/m)$. Thus the number of terms is

$$\frac{n_1! n_2! \cdots n_m!}{\prod\limits_n \prod\limits_{\mu(n/m)} (\nu^n_{1\mu}!)^{k_{\mu(n/m)}} \cdots (\nu^n_{m\mu}!)^{k_{\mu(n/m)}} k_{\mu(n/m)}!}. \tag{21}$$

Inserting equation (18) in equation (14), and taking into account equation (21) and the fact that $u_j^{n_j} = u_j^{(\sum_n \sum_{\mu(n/m)} k_{\mu(n/m)} \nu^n_{j\mu})} = \prod_n \prod_{\mu(n/m)} u_j^{k_{\mu(n/m)} \nu^n_{j\mu}}$ the functional (Eq. (14)) becomes

$$L\big[\{u\}\big] = 1 + \sum_m \sum_{\{m\}} \sum_s \sum_{\prod^s_m} \sum_{P_s} \prod_n \prod_{\mu(n/m)} \times \frac{1}{k_{\mu(n/m)}!} \left[\frac{\left(u_1^{\nu^n_{1\mu}} \cdots u_m^{\nu^n_{m\mu}} g_n(\nu^n_{1\mu} \cdots \nu^n_{m\mu}) \right)}{\nu^n_{1\mu}! \cdots \nu^n_{m\mu}!} \right]^{k_{\mu(n/m)}}. \tag{22}$$

This formidable expression can be rewritten in a simpler way as

$$L\big[\{u\}\big] = \prod_m \prod_{\{m\}} \prod_s \prod_{\prod^s_m} \sum_{k=0}^{\infty} \frac{1}{k!} \times \left[\frac{\left(u_1^{\nu^s_1} \cdots u_m^{\nu^s_m} g_s(\nu^s_1 \cdots \nu^s_m) \right)}{\nu^s_1! \cdots \nu^s_m!} \right]^k. \tag{23}$$

As a matter of fact each term of equation (23) can be put in one-to-one correspondence with a term of equation (22), with the aid of constraints (17, 19, 20).

It follows that

$$L\big[\{u\}\big] = \exp\left[\sum_m \sum_{\{m\}} \sum_s \sum_{\prod^s_m} \times \frac{\left(u_1^{\nu^s_1} \cdots u_m^{\nu^s_m} g_s(\nu^s_1 \cdots \nu^s_m) \right)}{(\nu^s_1! \cdots \nu^s_m!)} \right]. \tag{24}$$

On the basis of equation (24) it is possible to evaluate the probability, Q_0, that no dots of the i class be in the Δ_i domain, no dots of the j class be in the Δ_j domain etc. Let us denote by χ_i the characteristic function of the i-class dots, defined as follows: $\chi_i(\mathbf{x}) = 1$ for $\mathbf{x} \subset \Delta_i$ and $\chi_i(\mathbf{x}) = 0$ for $\mathbf{x} \not\subset \Delta_i$. Consequently, the stochastic variable "number of dots", N, reads $N^{(m)} = \sum_{\{1\}}^m \sum_{\langle 1 \rangle}^s \chi_i(\mathbf{x}_\nu)$. The average of the stochastic variable e^{ikN}, where k is a parameter, is given through equation (13) according to $\langle \exp(ikN) \rangle \equiv L\big[\{\exp(ik\chi) - 1\}\big]$. Moreover since $Q_0 = \lim\limits_{\exp(ik) \to 0} \langle \exp(ikN) \rangle$ [13] we infer from equation (14), the important relationship

$$Q_0 = L\big[\{-\chi\}\big] \tag{25}$$

which by employing equation (24), becomes

$$Q_0 = \exp\left[\sum_m \sum_{\{m\}} \sum_s \sum_{\prod^s_m} \times \frac{(-)^s \int\limits_{\Delta_1} d^{\nu^s_1}\mathbf{x}_1 \cdots \int\limits_{\Delta_m} d^{\nu^s_m}\mathbf{x}_m g_s(\nu^s_1 \cdots \nu^s_m)}{\nu^s_1! \cdots \nu^s_m!} \right]. \tag{26}$$

2.5 Continuum limit

In order to perform the continuum limit of equation (26) it is convenient to rewrite the CFs according to [14] as:

$$g_s(\nu^s_1, \nu^s_2, \cdots, \nu^s_m) = n_1^{\nu^s_1} n_2^{\nu^s_2} \cdots n_m^{\nu^s_m} \widetilde{g}_s \tag{27}$$

where $n_1, \cdots n_m$ are the densities of dots of classes $1, \cdots, m$, respectively. Moreover, it is possible to show that equation (26) can be rewritten as:

$$Q_0 = \exp\left[\sum_s \frac{(-)^s}{s!} \sum_{i_1} \cdots \sum_{i_s} (n_{i_1} \cdots n_{i_s}) \times \int\limits_{\Delta_{i_1}} d\mathbf{x}^{(i_1)} \cdots \int_{\Delta_{i_s}} d\mathbf{x}^{(i_s)} \widetilde{g}_s(\mathbf{x}^{(i_1)}, \cdots, \mathbf{x}^{(i_s)}) \right] \tag{28}$$

where the multiplicity (ν^s_i) is naturally included by reason of the fact that the sum indexes (i_k) run, independently, over all classes. In the Appendix C the equivalence of equations (26) and (28) is shown for the case of three classes. The continuum limit implies: $n_i \to \Delta n(t_i) = I(t_i)\Delta t$, $\Delta n(t_i)$ is the number of dots between the t_i and $t_i + \Delta t$ classes; thus equation (28) becomes

$$Q_0 = \exp\left\{ \sum_{s=1}^{\infty} \frac{(-)^s}{s!} \int_0^t dt_1 \int_0^t dt_2 \cdots \int_0^t dt_s I(t_1) \cdots I(t_s) \times \int_{\Delta_{t_1}} d\mathbf{x}_1 \cdots \int_{\Delta_{t_s}} d\mathbf{x}_s \, \widetilde{g}_s(\mathbf{x}_1 \cdots \mathbf{x}_s) \right\}. \tag{29}$$

It is worth noticing that in case of nucleation into an homogeneous medium, $\widetilde{g}_1 = 1$ and the contribution at $s = 1$, in the argument of equation (29), gives $-X_e = -\int_0^t dt' I(t')|\Delta_{t'}|$ where $|\Delta_{t'}|$ is the measure of the domain and X_e is the so called extended volume in dD. The kinetics can be rewritten according to:

$$Q_0 = \exp(-\gamma X_e) \tag{30}$$

where

$$\gamma = 1 - \sum_{s=2}^{\infty} \frac{(-)^s}{s! X_e} \int_0^t dt_1 \int_0^t dt_2 \cdots \int_0^t dt_s\, I(t_1) \cdots I(t_s) \times \int_{\Delta_{t_1}} d\mathbf{x}_1 \cdots \int_{\Delta_{t_s}} d\mathbf{x}_s\, \widetilde{g}_s(\mathbf{x}_1 \cdots \mathbf{x}_s). \tag{31}$$

Correlation among nuclei is entirely considered through the γ term and, in the limit $\gamma = 1$ equation (29) reduces to the one of the Poisson process. It is worth noticing that in the limiting case of simultaneous nucleation, *i.e.* for $I(t) \propto \delta(t)$ δ being Dirac's delta, equation (29) leads to the result obtained in reference [8].

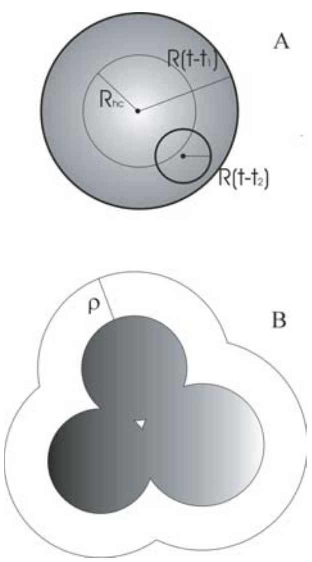

Fig. 1. Panel A refers to case I) of Section 3. The nucleation is prevented within a circle of radius R_{hc} centered around each nucleus. In the same panel it is also shown a phantom nucleus *i.e.* a nucleus born outside R_{hc} but beneath and already formed nucleus. In panel B a cluster made up of three nuclei is surrounded by a a zone of thickness ρ where the nucleation is forbidden. This refers to the correlation problem tackled in point II) of Section 3.

3 KJMA-type phase transitions case

The foregoing results can be exploited for describing phase transition kinetics in which nucleation and growth laws are given a priori (KJMA-type transitions). Although the theory is independent of the space dimension, for the sake of simplicity we will deal with the 2D case. To this end $I(t)$ becomes the nucleation rate, $|\Delta_{t'}| = \pi R^2(t-t')$, $R(t-t')$ being the growth law and $(1-Q_0)$ is equal to the fraction of transformed phase (surface).

Two cases can be pursued, they are:

a) the correlation functions do not depend on the birth time of the nuclei;
b) the correlation functions depend on the birth time of the nuclei.

The simplest example of correlation is the "hard core" case. For the a)-b) cases, as far as the lowest order term of $\widetilde{g}_2$ is concerned, the two dots "tilded" correlation functions are, respectively,

I)

$$\widetilde{g}_2^{(0)} = H(r - R_{hc}) - 1 \tag{32}$$

II)

$$\widetilde{g}_2^{(0)}(i,j) = H\big[r - (R_{ij} + \rho)\big] - 1 \tag{33}$$

where H is the Heaviside function, $r = |\mathbf{r}_1 - \mathbf{r}_2|$ is the modulus of the distance between nuclei 1 and 2, R_{hc} is the hard core distance, $R_{ij} = R(t_i - t_j)$ and ρ is, in general, a function of time. In other words around each island a region exists where nucleation is forbidden (Fig. 1). The first case (I) has been thoroughly analyzed in reference [1] by only considering terms up to $s = 2$, for constant nucleation rate and linear growth law. In particular, an analytical expression of the γ exponent has been given by decoupling the integral on the g_2 function in equation (31), once expressed through polar coordinates [1]. It is

$$\gamma(S_e, S^*) = 1 + \frac{1}{2}\left\{ S_e H\left(1 - \frac{3S_e}{S^*}\right) + \left[S^* - 2S_e (S^*/3S_e)^{3/2}\right] H\left(\frac{3S_e}{S^*} - 1\right) \right\} \tag{34}$$

where $S^* = \pi R_{hc}^2 I (3S_e/a^2\pi I)^{1/3}$, I and a being the nucleation and growth rates respectively. In this case the size of the zone where the nucleation is inhibited is constant and it is the same for each nucleus. Conversely, the second case is indeed more realistic since the capture zone is an annular ring of thickness ρ surrounding each nucleus. In other words, for a nucleus of radius R, the zone where the nucleation is inhibited, is a circle or radius $R + \rho$. This problem has been dealt with firstly in references [10,11] employing a different approach which is not based on the use of CFs. The formalism developed in Section 2 is general and can be applied to case II as well. By retaining terms up to $s = 2$ and considering a constant nucleation rate, equation (31) reads

$$\gamma = 1 + \frac{S_e}{2} - \frac{I^2}{2S_e} \int_0^t dt' \int_0^t dt''\, \Gamma\big[R(t,t'), R(t,t'')\big] \tag{35}$$

where, in case of linear growth,

$$\Gamma[R', R''] = 2\pi \int_0^{R''} r dr \int_0^{2\pi} d\theta \times \int_0^{\eta(R',r,\theta)} yH\big[y - (R' - R'' + \rho)\big] dy \quad (36)$$

where $\eta(R', r, \theta) = -r\cos\theta + (R'^2 - r^2 \sin^2\theta)^{1/2}$, ρ is considered as a constant and $R'' < R'$. The calculation points out that the contribution of equation (36) is numerically unimportant for $\rho > 0.7\left(\frac{a}{I}S_e\right)^{1/3}$ which, for $Se = 3$ that is its typical maximum value, gives $\rho > \left(\frac{a}{I}\right)^{1/3}$. So the following expression for the kinetics can be retained:

$$S \cong 1 - \exp\left(-S_e - \frac{S_e^2}{2}\right). \quad (37)$$

We conjecture that equation (37) can be employed whenever nuclei are correlated according to equation (33). Moreover in equation (37) the extended surface is computed using the actual nucleation rate which is an experimentally accessible quantity.

We recall that the for the hard core model (referred to as Matern's process) the exact expression of g_2 is available [15]. Conversely it is known that higher order correlation functions can be approximated only.

Apparently the aforementioned nucleation rate is unphysical the number of nucleation events being constant for each value of the surface fraction available for nucleation, S_{free}; a more suitable choice would require $I(t) = IS_{free}$.

It is worth pointing out that in case I), when the radius of the nucleus becomes larger than R_{hc}, the probability to nucleate a phantom is different from zero (Fig. 1A). On the contrary in case II) phantoms cannot nucleate at all. Furthermore, in the limiting case $\rho = 0$, the $S(t)$ kinetics given by equations (30, 35–36), reduces to the KJMA solution, but evaluated by using the actual nucleation rate. To be specific, the phase transition analyzed as a problem of correlated nucleation (nucleation is not permitted on the already transformed surface) with constant value of the actual nucleation rate, I, is stochastically equivalent to a KJMA problem for the non constant nucleation rate $I(t) = \frac{I}{(1-S)}$. In other words the difference between the two view points lays in the inclusion of phantoms as required in the KJMA treatment of phase transitions.

Conclusions

The exact solution for the kinetics of growth of spatially correlated nuclei for any nucleation function has been demonstrated in Section 2. It has been applied to model phase transition kinetics driven by a constant actual nucleation rate, when the correlation function depends on the birth time of the nucleus through the characteristic distance ρ. In this case phantoms do not exist and the kinetics reduces to equation (37) where the extended surface is computed on the actual nucleation rate. We conjecture that, in order to describe the kinetics of hard core correlated nuclei (Eq. (33)), the KJMA formula must be substituted by equation (37). Work is in progress to substantiate the conjecture.

Appendix A

The purpose of this appendix is to derive equations (11) and (12). In the first place we evaluate

$$\left\langle U^2 \right\rangle = \left\langle U^{(1)^2} \right\rangle_{\{1\}} + \left\langle U^{(2)^2} \right\rangle_{\{2\}} + \left\langle U^{(3)^2} \right\rangle_{\{3\}} + \cdots \quad (A.1)$$

Let us begin expanding the three terms of series (A.1)

$$U^{(1)^2} = \sum_{\langle 1\rangle} u_i \sum_{\langle 1\rangle} u_i = \sum_{\langle 1\rangle} u_i^2 + 2\sum_{\langle 2\rangle} u_i u_i; \quad (A.2)$$

$$U^{(2)^2} = \left(\sum_{\langle 1\rangle} u_i + \sum_{\langle 1\rangle} u_j\right)^2 = \left(\sum_{\langle 1\rangle} u_i\right)^2 + (j)^2 + 2\sum_{\langle 1\rangle} u_i \sum_{\langle 1\rangle} u_j = \left(\sum_{\langle 1\rangle} u_i^2 + 2\sum_{\langle 2\rangle} u_i u_i\right) + (j) + 2\sum_{\langle 1\rangle} u_i \sum_{\langle 1\rangle} u_j; \quad (A.3)$$

$$U^{(3)^2} = \left(\sum_{\langle 1\rangle} u_i + \sum_{\langle 1\rangle} u_j + \sum_{\langle 1\rangle} u_k\right)^2 = \left(\sum_{\langle 1\rangle} u_i\right)^2 + (j) + (k) + 2\sum_{\langle 1\rangle} u_i \sum_{\langle 1\rangle} u_j + (ik) + (jk) = \left(\sum_{\langle 1\rangle} u_i^2 + 2\sum_{\langle 2\rangle} u_i u_i\right) + (j) + (k) + 2\sum_{\langle 1\rangle} u_i \sum_{\langle 1\rangle} u_j + (ik) + (jk). \quad (A.4)$$

The addends made up by a letter (class index) in parenthesis denote, in a very short way, the same term on their left in which the class index is that in parenthesis. Regarding the evaluation of the averages they reduce to

$$\left\langle U^{(1)^2} \right\rangle_{\{1\}} = \sum_{\{1\}} (u_i^2 h_i) \sum_{\{1\}} (u_i u_i h_{ii}) \quad (A.5)$$

where $h_{ii} \equiv \sum_i \sum_{\prod_i^s} \frac{n_i(n_i-1)}{n_i!} \int Q^{(1)}_{\pi_i^s} d^{s-2}\mathbf{x}_i$,

$$\left\langle U^{(2)^2} \right\rangle_{\{2\}} = \sum_{\{1\}} \sum_{\{1\}\backslash i} (u_i^2 h_{i,j}) + \sum_{\{1\}} \sum_{\{1\}\backslash i} (u_i u_i h_{ii,j}) + 2 \sum_{\{2\}} (u_i u_j h_{ij}) \quad \text{(A.6)}$$

where $h_{ii,j} \equiv \sum_s \sum_{\prod_{\{2\}}^s} \frac{n_i(n_i-1)}{n_i! n_j!} \int Q^{(2)}_{\pi_{ij}^s} d^{n_i-2}\,\mathbf{x}_i\, d^{n_j}\,\mathbf{x}_j$ and $h_{ij} \equiv \sum_s \sum_{\prod_{\{2\}}^s} \frac{n_i n_j}{n_i! n_j!} \int Q^{(2)}_{\pi_{ij}^s} d^{n_i-1}\,\mathbf{x}_i\, d^{n_j-1}\mathbf{x}_j$. Since $2\sum_{\{2\}}(u_i u_j h_{ij}) = \sum_{\{1\}} \sum_{\{1\}\backslash i} (u_i u_j h_{ij})$, equation (A.6) can be also written as

$$\left\langle U^{(2)^2} \right\rangle_{ij} = \sum_{\{1\}} \sum_{\{1\}\backslash i} \left[(u_i^2 h_{i,j}) + (u_i u_i h_{ii,j}) + (u_i u_j h_{ij}) \right]. \quad \text{(A.7)}$$

As far as $\left\langle U^{(3)^2} \right\rangle_{\{3\}}$ is concerned

$$\left\langle U^{(3)^2} \right\rangle_{\{3\}} = \sum_{\{3\}} \left[(u_i^2 h_{i,jk}) + (j) + (k) + (u_i u_i h_{ii,jk}) + (j) + (k) \right] + 2 \sum_{\{3\}} \left[(u_i u_j h_{ij,k}) + (ki) + (jk) \right] \quad \text{(A.8)}$$

or

$$\left\langle U^{(3)^2} \right\rangle_{\{3\}} = \sum_{\{1\}} \sum_{\{2\}\backslash i} \left[(u_i^2 h_{i,jk}) + (u_i u_i h_{ii,jk}) \right] + \sum_{\{1\}} \sum_{\{1\}\backslash i} \sum_{\{1\}\backslash i.j} (u_i u_j h_{ij,k}) \quad \text{(A.9)}$$

where

$$h_{ii,jk} \equiv \sum_s \sum_{\prod_{\{3\}}^s} \frac{n_i(n_i-1)}{n_i! n_j! n_k!} \int Q^{(3)}_{\pi_{ijk}^s} d^{n_i-2}\,\mathbf{x}_i\, d^{n_j}\,\mathbf{x}_j\, d^{n_k}\,\mathbf{x}_k$$

and

$$h_{ij,k} \equiv \sum_s \sum_{\prod_{\{3\}}^s} \frac{n_i n_j}{n_i! n_j! n_k!} \int Q^{(3)}_{\pi_{ijk}^s} d^{n_i-1}\,\mathbf{x}_i\, d^{n_j-1}\,\mathbf{x}_j\, d^{n_k}\,\mathbf{x}_k.$$

Combining equations (A.5, A.7, A.9) the average of U^2 is at last achieved

$$\begin{aligned} \left\langle U^2 \right\rangle &= \sum_{\{1\}} (u_i^2 h_i) + \sum_{\{1\}} (u_i u_i h_{ii}) \\ &+ \sum_{\{1\}} \sum_{\{1\}\backslash i} \left[(u_i^2 h_{i,j}) + (u_i u_i h_{ii,j}) + (u_i u_j h_{ij}) \right] \\ &+ \sum_{\{1\}} \sum_{\{2\}\backslash i} \left[(u_i^2 h_{i,jk}) + (u_i u_i h_{ii,jk}) \right] \\ &+ \sum_{\{1\}} \sum_{\{1\}\backslash i} \sum_{\{1\}\backslash i.j} (u_i u_j h_{ij,k}) \\ &= \sum_{\{1\}} \left[\left(u_i^2 \left\{ h_i + \sum_{\{1\}\backslash i} h_{i,j} + \sum_{\{2\}\backslash i} h_{i,jk} + \cdots \right\} \right) \right. \\ &+ \left(u_i u_i \left\{ h_{ii} + \sum_{\{1\}\backslash i} h_{ii,j} + \sum_{\{2\}\backslash i} h_{ii,jk} + \cdots \right\} \right) \\ &+ \left. \sum_{\{1\}\backslash i} \left(u_i u_j \left\{ h_{ij} + \sum_{\{1\}\backslash i.j} h_{ij,k} \right\} \right) \right]. \end{aligned} \quad \text{(A.10)}$$

By defining the *f*-functions for any couple of classes as

$$f_{ii} \equiv h_{ii} + \sum_{\{1\}\backslash i} h_{ii,j} + \sum_{\{2\}\backslash i} h_{ii,jk} + \sum_{\{3\}\backslash i} h_{ii,jkl} + \cdots \quad \text{(A.11)}$$

$$f_{ij} \equiv h_{ij} + \sum_{\{1\}\backslash i,j} h_{ij,k} + \cdots \quad \text{(A.12)}$$

equation (A.10) finally gives

$$\left\langle U^2 \right\rangle = \sum_{\{1\}} (u_i^2 f_i) + \sum_{\{1\}} \sum_{\{1\}} (u_i u_j f_{ij}). \quad \text{(A.13)}$$

Concerning the calculation of

$$\left\langle U^3 \right\rangle = \left\langle U^{(1)^3} \right\rangle_{\{1\}} + \left\langle U^{(2)^3} \right\rangle_{\{2\}} + \left\langle U^{(3)^3} \right\rangle_{\{3\}} + \cdots, \quad \text{(A.14)}$$

let us begin expanding the first three terms of the series (A.14):

$$\begin{aligned} U^{(1)^3} &= \sum_{\langle 1 \rangle} u_i \sum_{\langle 1 \rangle} u_i \sum_{\langle 1 \rangle} u_i \\ &= \sum_{\langle 1 \rangle} u_i^3 + 3 \sum_{\langle 2 \rangle} u_i^2 u_i + 3! \sum_{\langle 3 \rangle} u_i u_i u_i; \end{aligned} \quad \text{(A.15)}$$

$$U^{(2)^3} = \Big(\sum_{\langle 1\rangle} u_i + \sum_{\langle 1\rangle} u_j\Big)^3 = \Big(\sum_{\langle 1\rangle} u_i\Big)^3 + (j) + 3\Big(\sum_{\langle 1\rangle} u_i\Big)^2 \sum_{\langle 1\rangle} u_j + (ij)$$
$$= \Big(\sum_{\langle 1\rangle} u_i^3 + 3\sum_{\langle 2\rangle} u_i^2 u_i + 3!\sum_{\langle 3\rangle} u_i u_i u_i\Big) + (j) + 3\Big(\sum_{\langle 1\rangle} u_i^2 + 2\sum_{\langle 2\rangle} u_i u_i\Big)\sum_{\langle 1\rangle} u_j + (ji); \quad \text{(A.16)}$$

$$U^{(3)^3} = \Big(\sum_{\langle 1\rangle} u_i + \sum_{\langle 1\rangle} u_j + \sum_{\langle 1\rangle} u_k\Big)^3 = \Big(\sum_{\langle 1\rangle} u_i\Big)^3 + (j) + (k) + 3\Big(\sum_{\langle 1\rangle} u_i\Big)^2 \sum_{\langle 1\rangle} u_j + (ik) + (jk)$$
$$+ 3\sum_{\langle 1\rangle} u_i \Big(\sum_{\langle 1\rangle} u_j\Big)^2 + (ik) + (jk) + 6\sum_{\langle 1\rangle} u_i + \sum_{\langle 1\rangle} u_j + \sum_{\langle 1\rangle} u_k$$
$$= \Big(\sum_{\langle 1\rangle} u_i^3 + 3\sum_{\langle 2\rangle} u_i^2 u_i + 3!\sum_{\langle 3\rangle} u_i u_i u_i\Big) + (j) + (k) + 3\Big(\sum_{\langle 1\rangle} u_i^2 + 2\sum_{\langle 2\rangle} u_i u_i\Big)\sum_{\langle 1\rangle} u_j + (ik) + (jk)$$
$$+ 3\sum_{\langle 1\rangle} u_i \Big(\sum_{\langle 1\rangle} u_j^2 + 2\sum_{\langle 2\rangle} u_j u_j\Big) + (ik) + (jk) + 6\sum_{\langle 1\rangle} u_i \sum_{\langle 1\rangle} u_j \sum_{\langle 1\rangle} u_k. \quad \text{(A.17)}$$

The averages are:

$$\Big\langle U^{(1)^3}\Big\rangle_{\{1\}} = \sum_{\{1\}} (u_i^3 h_i) + 3\sum_{\{1\}} (u_i^2 u_i h_{ii}) + \sum_{\{1\}} (u_i u_i u_i h_{iii}) \quad \text{(A.18)}$$

where

$$h_{iii} = \sum_s \sum_{\prod_i^s} \frac{n_i(n_i-1)(n_i-2)}{n_i!} \int Q^{(1)}_{\pi_i^s} d^{s-3}\,\mathbf{x}_i;$$

$$\Big\langle U^{(2)^3}\Big\rangle_{\{2\}} = \sum_{\{1\}} \sum_{\{1\}\backslash i} \Big[(u_i^3 h_{i,j}) + 3(u_i^2 u_i h_{ii,j}) + (u_i u_i u_i h_{iii,j})\Big] + \Big\langle 3\Big(\sum_{\{1\}} u_i^2 + 2\sum_{\{2\}} u_i u_i\Big)\sum_{\{1\}} u_j + (ji)\Big\rangle_{\{2\}} \quad \text{(A.19)}$$

and the computation of the last two terms leads to

$$\Big\langle 3\sum_{\langle 1\rangle} u_i^2 \sum_{\langle 1\rangle} u_j + (ji)\Big\rangle_{\{2\}} = 3\sum_{\{2\}} \Big[(u_i^2 u_j h_{ij}) + (u_j^2 u_i h_{ji})\Big] = 3\sum_{\{1\}} \sum_{\{1\}\backslash i} (u_i^2 u_j h_{ij}) \quad \text{(A.20)}$$

and

$$\Big\langle 3 \times 2\sum_{\langle 2\rangle} u_i u_i \sum_{\langle 1\rangle} u_j + (ji)\Big\rangle_{\{2\}} = 3\sum_{\{2\}} \Big[\big(u_i u_i u_j h_{iij}\big) + \big(u_j u_j u_i h_{jji}\big)\Big] = 3\sum_{\{1\}} \sum_{\{1\}\backslash i} \big(u_i u_i u_j h_{iij}\big). \quad \text{(A.21)}$$

Combining equation (A.19–A.21) the average $\Big\langle U^{(2)^3}\Big\rangle_{\{2\}}$ reduces to

$$\Big\langle U^{(2)^3}\Big\rangle_{\{2\}} = \sum_{\{1\}} \sum_{\{1\}\backslash i} \Big[\big(u_i^3 h_{i,j}\big) + 3\big(u_i^2 u_i h_{ii,j}\big) + \big(u_i u_i u_i h_{iii,j}\big) + 3\big(u_i^2 u_j h_{ij}\big) + 3\big(u_i u_i u_j h_{iij}\big)\Big]. \quad \text{(A.22)}$$

For the sake of clarity, in calculating $\Big\langle U^{(3)^3}\Big\rangle$ it is convenient to proceed considering the last term of equation (A.17) line by line.

The three sums over $\langle 1\rangle$, $\langle 2\rangle$ and $\langle 3\rangle$ of the first line lead, considering also the contribution of (j) and (k), respectively, to $\sum_{\{1\}} \sum_{\{2\}\backslash i} (u_i^3 h_{i,jk})$, $3\sum_{\{1\}} \sum_{\{2\}\backslash i} \big(u_i^2 u_i h_{ii,j}\big)$ and $\sum_{\{1\}} \sum_{\{2\}\backslash i} \big(u_i u_i u_i h_{iii,jk}\big)$. To obtain these relations it has been exploited the equality: $\sum_{\{3\}}[(i,jk)+(j,ik)+(k,ij)] = \sum_{\{1\}}\sum_{\{2\}\backslash i}(i,jk)$. Therefore the contribution of the entire first line is

$$\sum_{\{1\}}\sum_{\{2\}\backslash i}\Big[\big(u_i^3 h_{i,jk}\big)+3\big(u_i^2 u_i h_{ii,jk}\big)+\big(u_i u_i u_i h_{iii,jk}\big)\Big]. \tag{A.23}$$

Concerning the second line, let us begin considering the average of $3\sum_{\langle 1\rangle} u_i^2 \sum_{\langle 1\rangle} u_j$ and of the analogous terms (ik) e (jk); they lead to $3\sum_{\{3\}}\big[\big(u_i^2 u_j h_{ij,k}\big)+\big(u_i^2 u_k h_{ik,j}\big)+\big(u_j^2 u_k h_{jk,i}\big)\big]$ and from the same terms in the third line one gets $3\sum_{\{3\}}\big[\big(u_j^2 u_i h_{ji,k}\big)+\big(u_k^2 u_i h_{ki,j}\big)+\big(u_k^2 u_j h_{kj,i}\big)\big]$. Since $\big(u_i^2 u_j h_{ij,k}\big)=\big(u_j^2 u_i h_{ji,k}\big)$ the two contributions can sum up to

$$3\times 2\sum_{\{3\}}\Big[\big(u_i^2 u_j h_{ij,k}\big)+\big(u_i^2 u_k h_{ik,j}\big)+\big(u_j^2 u_k h_{jk,i}\big)\Big] \tag{A.24}$$

and, because of the equality $2\sum_{\{3\}}\big[(ij,k)+(ik,j)+(jk,i)\big] = \sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}(ij,k)$, equation (A.24) becomes

$$3\sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}(u_i^2 u_j h_{ij,k}). \tag{A.25}$$

Similarly, the term $3\times 2\sum_{\langle 2\rangle} u_i u_i \sum_{\langle 1\rangle} u_j$ together with the analogous terms (ik) e (jk) lead to

$$3\sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}(u_i u_i u_j h_{iij,k}). \tag{A.26}$$

The forth line yields

$$6\sum_{\{3\}}(u_i u_j u_k h_{ijk}) = \sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}(u_i u_j u_k h_{ijk}). \tag{A.27}$$

Summing up equations (A.23) and (A.25–A.27) one gets

$$\begin{aligned}\Big\langle U^{(3)^3}\Big\rangle_{\{3\}} =& \sum_{\{1\}}\sum_{\{2\}\backslash i}\Big[\big(u_i^3 h_{i,jk}\big)+3\big(u_i^2 u_i h_{ii,jk}\big)\\ &+\big(u_i u_i u_i h_{iii,jk}\big)\Big]+\sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}\Big[3\big(u_i^2 u_j h_{ij,k}\big)\\ &+3\big(u_i u_i u_j h_{iij,k}\big)+\big(u_i u_j u_k h_{ijk}\big)\Big]\end{aligned} \tag{A.28}$$

and combining equations (A.18, A.22) and (A.28) the average of U^3 is at last obtained

$$\begin{aligned}\Big\langle U^3\Big\rangle =& \sum_{\{1\}}\Big[\big(u_i^3 h_i\big)+3\big(u_i^2 u_i h_{ii}\big)+\big(u_i u_i u_i h_{iii}\big)\Big]\\ &+\sum_{\{1\}}\sum_{\{1\}\backslash i}\Big[\big(u_i^3 h_{i,j}\big)+3\big(u_i^2 u_i h_{ii,j}\big)\\ &+\big(u_i u_i u_i h_{iii,j}\big)+3\big(u_i^2 u_j h_{ij}\big)+3\big(u_i u_i u_j h_{iij}\big)\Big]\\ &+\sum_{\{1\}}\sum_{\{2\}\backslash i}\Big[\big(u_i^3 h_{i,jk}\big)+3\big(u_i^2 u_i h_{ii,jk}\big)+\big(u_i u_i u_i h_{iii,jk}\big)\Big]\\ &+\sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}\Big[3\big(u_i^2 u_j h_{ij,k}\big)+3\big(u_i u_i u_j h_{iij,k}\big)\\ &+\big(u_i u_j u_k h_{ijk}\big)\Big]\\ =& \sum_{\{1\}}\bigg\{\Big(u_i^3\big(h_i+\sum_{\{1\}\backslash i}h_{i,j}+\sum_{\{2\}\backslash i}h_{i,jk}+\cdots\big)\Big)\\ &+\Big(u_i^2 u_i\big(3h_{ii}+3\sum_{\{1\}\backslash i}h_{ii,j}+3\sum_{\{2\}\backslash i}h_{ii,jk}+\cdots\big)\Big)\\ &+\Big(u_i u_i u_i\big(h_{iii}+\sum_{\{1\}\backslash i}h_{iii,j}+\sum_{\{2\}\backslash i}h_{iii,jk}+\cdots\big)\Big)\\ &+3\sum_{\{1\}\backslash i}\Big[\Big(u_i^2 u_j\big(h_{ij}+\sum_{\{1\}\backslash i,j}h_{ij,k}+\cdots\big)\\ &+\Big(u_i u_i u_j\big(h_{iij}+\sum_{\{1\}\backslash i,j}h_{iij,k}+\cdots\big)\Big]\\ &+\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}\Big(u_i u_j u_k\big(h_{ijk}+\cdots\big)\Big)\bigg\}\\ =& \sum_{\{1\}}\bigg\{\big(u_i^3 f_i\big)+3\big(u_i^2 u_i f_{ii}\big)+\big(u_i u_i u_i f_{iii}\big)\\ &+3\sum_{\{1\}\backslash i}\Big[\big(u_i^2 u_j f_{ij}\big)+\big(u_i u_i u_j f_{iij}\big)\\ &+\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}\big(u_i u_j u_k f_{ijk}\big)\bigg\}.\end{aligned} \tag{A.29}$$

In writing the last term of equation (A29) the following f-functions have been defined for any tern of classes as

$$f_{iii} = h_{iii}+\sum_{\{1\}\backslash i}h_{iii,j}+\sum_{\{2\}\backslash i}h_{iii,jk}+\cdots \tag{A.30}$$

$$f_{iij} = h_{iij}+\sum_{\{1\}\backslash i,j}h_{iij,k}+\cdots \tag{A.31}$$

$$f_{ijk} = h_{ijk}+\cdots \tag{A.32}$$

It is easy to verify that equation (A.29) can be rewritten in a more compact form as

$$\left\langle U^3\right\rangle = \sum_{\{1\}}\left(u_i^3 f_i\right) + 3\sum_{\{1\}}\sum_{\{1\}}\left(u_i^2 u_j f_{ij}\right) + \sum_{\{1\}}\sum_{\{1\}}\sum_{\{1\}}\left(u_i u_j u_k f_{ijk}\right). \quad (A.33)$$

Appendix B

In case of a single class equation (13) becomes $\left\langle\prod_{\langle 1\rangle}^{n_i}(1+u_i)\right\rangle = \left\langle 1+\sum_{\langle 1\rangle} u_i + \sum_{\langle 2\rangle} u_i u_i + \sum_{\langle 3\rangle} u_i u_i u_i + \cdots\right\rangle$ and by exploiting the results obtained in calculating the averages of the variable U and its powers, it is possible to verify that the average operation on the functional gives

$$\left\langle\sum_{\langle 1\rangle} u_i\right\rangle = \sum_{\{1\}}\left(u_i h_i\right) \quad (B.1')$$

$$\left\langle\sum_{\langle 2\rangle} u_i u_i\right\rangle = \frac{1}{2!}\sum_{\{1\}}\left(u_i u_i h_{ii}\right) \quad (B.2')$$

$$\left\langle\sum_{\langle 2\rangle} u_i u_i u_i\right\rangle = \frac{1}{3!}\sum_{\{1\}}\left(u_i u_i u_i h_{iii}\right). \quad (B.3')$$

In case of two classes equation (13) reduces to;

$$\left\langle\prod_{\langle 1\rangle}^{n_i}(1+u_i)\prod_{\langle 1\rangle}^{n_j}(1+u_j)\right\rangle = \left\langle 1+\sum_{\langle 1\rangle} u_i + \sum_{\langle 1\rangle} u_j + \sum_{\langle 2\rangle} u_i u_i + \sum_{\langle 2\rangle} u_j u_j + \sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_i u_j + \sum_{\langle 3\rangle} u_i u_i u_i + \sum_{\langle 2\rangle}\sum_{\langle 1\rangle} u_i u_i u_j + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_i u_j u_j + \cdots\right\rangle$$

and averaging

$$\left\langle\sum_{\langle 1\rangle} u_i + \sum_{\langle 1\rangle} u_j\right\rangle = \sum_{\{1\}}\sum_{\{1\}\backslash i}\left(u_i h_{i,j}\right) \quad (B.1'')$$

$$\left\langle\sum_{\langle 2\rangle} u_i u_i + \sum_{\langle 2\rangle} u_j u_j\right\rangle = \frac{1}{2!}\sum_{\{1\}}\sum_{\{1\}\backslash i}\left(u_i u_i h_{ii,j}\right) \quad (B.2'')$$

$$\left\langle\sum_{\langle 3\rangle} u_i u_i u_i + \sum_{\langle 3\rangle} u_j u_j u_j\right\rangle = \frac{1}{3!}\sum_{\{1\}}\sum_{\{1\}\backslash i}\left(u_i u_i u_i h_{iii,j}\right) \quad (B.3'')$$

$$\left\langle\sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_i u_j\right\rangle = \frac{1}{2}\sum_{\{1\}}\sum_{\{1\}\backslash i}\left(u_i u_j h_{ij}\right) = \sum_{\{2\}}\left(u_i u_j h_{ij}\right) \quad (B.4'')$$

$$\left\langle\sum_{\langle 2\rangle}\sum_{\langle 1\rangle} u_i u_i u_j + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_i u_j u_j\right\rangle = \frac{1}{2!}\sum_{\{1\}}\sum_{\{1\}\backslash i}\left(u_i u_i u_j h_{iij}\right). \quad (B.5'')$$

In case of three classes equation (13) reduces to

$$\left\langle\prod_{\langle 1\rangle}^{n_i}(1+u_i)\prod_{\langle 1\rangle}^{n_j}(1+u_j)\prod_{\langle 1\rangle}^{n_k}(1+u_k)\right\rangle = \left\langle 1+\sum_{\langle 1\rangle} u_i+\sum_{\langle 1\rangle} u_j + \sum_{\langle 1\rangle} u_k + \sum_{\langle 2\rangle} u_i u_i + \sum_{\langle 2\rangle} u_j u_j + \sum_{\langle 2\rangle} u_k u_k + \sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_i u_j + \sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_i u_k + \sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_j u_k + \sum_{\langle 3\rangle} u_i u_i u_i + \sum_{\langle 3\rangle} u_j u_j u_j + \sum_{\langle 3\rangle} u_k u_k u_k + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_i u_i u_j + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_i u_i u_k + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_j u_j u_i + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_j u_j u_k + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_k u_k u_j + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_k u_k u_i + \sum_{\langle 1\rangle}\sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_i u_j u_k + \cdots\right\rangle$$

and averaging

$$\left\langle\sum_{\langle 1\rangle} u_i + \sum_{\langle 1\rangle} u_j + \sum_{\langle 1\rangle} u_k\right\rangle = \sum_{\{1\}}\sum_{\{2\}\backslash i}\left(u_i h_{i,jk}\right) \quad (B.1''')$$

$$\left\langle\sum_{\langle 2\rangle} u_i u_i + \sum_{\langle 2\rangle} u_j u_j + \sum_{\langle 2\rangle} u_k u_k\right\rangle = \frac{1}{2}\sum_{\{1\}}\sum_{\{2\}\backslash i}\left(u_i u_i h_{ii,jk}\right) \quad (B.2''')$$

$$\sum_{\langle 3\rangle} u_i u_i u_i + \sum_{\langle 3\rangle} u_j u_j u_j + \sum_{\langle 3\rangle} u_k u_k u_k\Bigg\rangle = \frac{1}{3!}\sum_{\{1\}}\sum_{\{2\}\backslash i}\left(u_i u_i u_i h_{iii,jk}\right) \quad (B.3''')$$

$$\left\langle\sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_i u_j + \sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_i u_k + \sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_j u_k\right\rangle = \frac{1}{2}\sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}\left(u_i u_j h_{ij,k}\right) = \sum_{\{3\}}\left(u_i u_j h_{ij,k}\right) \quad (B.4''')$$

$$\left\langle\sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_i u_i u_j + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_i u_i u_k + \cdots + \sum_{\langle 1\rangle}\sum_{\langle 2\rangle} u_k u_k u_i\right\rangle = \frac{1}{2}\sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}\left(u_i u_i u_j h_{iij,k}\right) \quad (B.5''')$$

$$\left\langle \sum_{\langle 1\rangle}\sum_{\langle 1\rangle}\sum_{\langle 1\rangle} u_i u_j u_k \right\rangle = \frac{1}{6}\sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}\left(u_i u_j u_k h_{ijk}\right). \tag{B.6'''}$$

It is recognized that, once summed, equations (B.1) lead to $\sum_{\{1\}}\left(u_i f_i\right)$, equations (B.2) lead to $\frac{1}{2!}\sum_{\{1\}}\left(u_i u_i f_{ii}\right)$, equations (B.3) lead to $\frac{1}{3!}\sum_{\{1\}}\left(u_i u_i u_i f_{iii}\right)$, equations (B.4) lead to $\frac{1}{2}\sum_{\{1\}}\sum_{\{1\}\backslash i}\left(u_i u_j f_{ij}\right) = \sum_{\{2\}}\left(u_i u_j f_{ij}\right)$, equations (B.5) lead to $\frac{1}{2!}\sum_{\{1\}}\sum_{\{1\}\backslash i}\left(u_i u_i u_j f_{iij}\right)$ and equation (B.6) leads to $\frac{1}{3!}\sum_{\{1\}}\sum_{\{1\}\backslash i}\sum_{\{1\}\backslash i,j}\left(u_i u_j u_k f_{ijk}\right) = \sum_{\{3\}}\left(u_i u_j u_k f_{ijk}\right)$. In other words, the average of the functional equation (13) becomes

$$\begin{aligned} L[\{u\}] = 1 &+ \sum_{\{1\}}\left(u_i f_i\right) + \frac{1}{2!}\sum_{\{1\}}\left(u_i u_i f_{ii}\right) \\ &+ \frac{1}{3!}\sum_{\{1\}}\left(u_i u_i u_i f_{iii}\right) + \sum_{\{2\}}\left(u_i u_j f_{ij}\right) \\ &+ \frac{1}{2!}\sum_{\{1\}}\sum_{\{1\}\backslash i}\left(u_i u_i u_j f_{iij}\right) + \sum_{\{3\}}\left(u_i u_j u_k f_{ijk}\right) + \cdots \end{aligned} \tag{B.7}$$

It is possible to rewrite equation (B.7) in a more familiar and manageable form as reported in equation (14).

Appendix C

In order to demonstrate the equivalence between equations (26) and (28), we will tackle the case $m = 3$. For $m > 3$ the same path of computation can be followed. Let us single out the contribution $s = 3$ from equation (26). It is

$$\begin{aligned} T_3 &= \sum_{m=1}^{3}\sum_{\{m\}}\sum_{\prod_m^3}\frac{-I_3^{\{m\}}}{\nu_1^3!\cdots\nu_1^m!} \\ &= -\left(\sum_{\{1\}}\frac{I_3^{(1)}}{3!} + \sum_{\{2\}}\left[\frac{I_3^{(2,1)}}{2!1!} + \frac{I_3^{(1,2)}}{2!1!}\right] + \sum_{\{3\}}\frac{I_3^{(3)}}{1!1!1!}\right) \end{aligned} \tag{C.1}$$

that, for the sake of computation convenience, can be rewritten as

$$\begin{aligned} T_3 &= -\left(\sum_i \frac{I_3^{(i,i,i)}}{3!} + \sum_{i>j}\left[\frac{I_3^{(i,i,j)}}{2!} + \frac{I_3^{(j,j,i)}}{2!}\right] + \sum_{i>j>k} I_3^{(i,j,k)}\right) \\ &= -\left(\sum_i \frac{I_3^{(i,i,i)}}{3!} + \sum_{i\neq j}\left[\frac{I_3^{(i,i,j)}}{2!}\right] + \frac{1}{3!}\sum_{i\neq j\neq k} I_3^{(i,j,k)}\right). \end{aligned} \tag{C.2}$$

Equation (28) yields, for $s = 3$,

$$\begin{aligned} T_3' &= \frac{1}{3!}\sum_{(i,j,k)} I_3^{(i,j,k)} \\ &= \frac{1}{3!}\Big[\sum_i I_3^{(i,i,i)} + 3\sum_{i\neq j} I_3^{(i,i,j)} + \sum_{i\neq j\neq k} I_3^{(i,j,k)}\Big] \end{aligned} \tag{C.3}$$

apparently $T_3 = T_3'$.

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