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INFLUENCE OF THE GROWTH PROCESS ON SOME LAWS
DEDUCED FROM PERCOLATION THEORY *

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ABSTRACT

A brutal application of the percolation theory to some physical problems can lead to erroneous interpretation of the experimental results. Among these problems, the influence of the growth process on the percolation laws is studied. The behaviour of $n_s(t)$, the number of clusters of size s , at time t , is analyzed and linked to a macroscopic property of the system for a comparison to experimental laws.

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I. INTRODUCTION

During these last years, a lot of studies have made use of the notion introduced by the percolation theory, to explain the behaviour of the physical properties of inhomogeneous medium [1-6].

On a conceptual point of view, some mediums show off serious difficulties due, on the one hand, to the brutal application of the percolation results, and on the other, to the comprehension of the disorder notion present in these mediums. Among these problems we note the nucleation systems, and particularly the condensed nucleation systems. Theoretical studies allow to give, for example, the mean number of crystallites for a given sample [7-19].

Direct [19,20] and indirect experimental studies [21-28] have been established to explain the morphologies and the kinetics of crystallization for these systems. In the same way, numerical simulations were done to study the growth of the dendrites and spherulites [29,30].

The aim of the paper is to show that the percolation theory results can help us to give a phenomenological description of the structural aspects of these systems. Such a work implies the comprehension of the physical limits of the nucleation and percolation problems. Unfortunately, we have not found, for example, statistical results ascribed to experimental data, which give us the number of crystallites in the sense of the percolation. Nevertheless, a comparison will be possible in evaluating the transformed volume fraction $x(t)$.

II. THEORETICAL RESULTS

Nucleation systems and percolation

Nucleation reflects the apparition of embryos (germs or nucleus) having a given structure, different from that of the sea of sites (or atoms) in which they wet. The condensed nucleation systems present two phases; the evolution of the amorphous state (critical phase) towards the crystalline state (final phase) is an irreversible transformation.

The formation of clusters - s , (e.g., crystallites with s sites) is governed by two fundamental processes.

i) the germination process which consists of the apparition of microcrystals aleatory distributed. These germs and the massive crystalline state are supposed to present the same physical properties.

ii) the growth process characterizing the interaction between the peripheric atoms of the crystallite and those of the amorphous sea. Although this process takes place in the same way as germination, it is not a genuine stochastic phenomenon.

In elementary percolation theory, the medium is considered like mathematical systems of infinite dimensionality with non-interacting sites. So, if the germination which consists in a stochastic generation of sites exists in the percolation theory, by contrast, the "regular" growth phenomenon has no sense. In other terms, the influence of the growth process would condition the convergence of the physical limits of these two models.

Theoretical models

It is interesting to see principal theoretical results elaborated to understand the structural properties of the nucleation systems.

We find first the classical theory of Becker-Döring [11] which considers the formation of droplets from a supersaturated vapour. The mean number of clusters - s (or droplets with s molecules) is given by

$$m_s = q_0 \exp \left(- \Delta\mu \cdot b - B s^{1-1/d} \right) \quad (1)$$

where q_0 is the initial number of monomers; $\Delta\mu$ is the difference of the chemical potential between the two phases; B is a normalized surface tension, and d is the dimensionality.

The use of the Fischer model was then suggested [12]

$$m_s = q_0 s^{-(2+\frac{1}{\sigma})} \exp \left(- \Delta\mu \cdot s - b \left(1 - \frac{T_c}{T} \right) s^\sigma \right) \quad (2)$$

where q_0 and b are constants, δ and σ are critical exponents, T and T_c the temperature of the sample and the critical temperature.

It has also been shown [13] that

$$m_s(p) = q_0 s^{-2} \tilde{m} \left(\epsilon s^\sigma, \Delta\mu \cdot s \right) \quad (3)$$

with $\epsilon = \frac{p-p_c}{p_c}$, where p and p_c are, respectively, the probability for a site to be occupied or empty, and the critical probability, and $\tilde{m}(\epsilon s^\sigma, \Delta\mu \cdot s)$ is a scaling function.

Then we found the scaling theory [15-18] which gives

$$m_s(p) = q_0 s^{-2} \exp \left[-q_1 \epsilon^\Delta \cdot s^{n_{1,2}} \right] \quad (4a)$$

with

$$n_{1,2} = \begin{cases} 1-1/d & \text{for } p < p_c \\ 1 & \text{for } p > p_c \end{cases} \quad (4b)$$

q_0 and q_1 are constant parameters. The relation (4a) is given for $s \rightarrow \infty$. For small values of s, and for $p < p_c$ the contribution is given by [14]

$$m_s(p) = q_0 s^{-2} \exp \left\{ -q_1 \epsilon^\Delta s^\sigma - q_2 s^u \right\} \quad (5)$$

with q_0 , q_1 and q_2 constant.

So, as it can be seen, the mean number of clusters - s is generally written as

$$m_s(p) = q_0 s^{-2} \exp \left\{ -q_1 \epsilon^\Delta s^{n_{1,2}} - q_2 s^u \right\} \quad (6)$$

This form of variation contains a pre-exponential term $q_0 s^{-2}$, a transition term $q_1 \epsilon^\Delta s^{n_{1,2}}$, and a non-transition term $q_2 s^u$ which expresses the analytical behaviour of the background.

III. EXPERIMENTAL MODELS

Several studies are reported giving some features of these systems. Direct observations [19,20] allow us to evaluate the nucleation and germination rates.

Indirect measures of conductivities and photoconductivities have been attempted to understand the morphologies and the kinetics of crystallization of given systems, and thereby the determination of the crystallized (or transformed) volume fraction $x(t)$.

Among these models, we distinguish Germain *et al.* [21-25] who considers the variation of conductivity given by Landauer [26]

$$\frac{1}{1 - \alpha_G} = 1 - f_G(t) \quad (7 a)$$

and

$$f_G(t) = \frac{(\sigma_a - \sigma_t)(\sigma_c + 2\sigma_t)}{(\sigma_c - \sigma_t)(\sigma_a + 2\sigma_t)} \quad (7 b)$$

where σ_a , σ_c and σ_t are, respectively, the conductivities for the amorphous state, the crystalline state and the mixture at time t .

The experimental data of conductivities combined with the last relations lead to an Avrami relation form for the fraction $\alpha_G(t)$, as

$$\alpha_G(t) = 1 - \exp \left\{ - \sum_{r=1}^4 K_r \cdot t^r \right\} \quad (8)$$

where K_r are coefficients depending on temperatures, r being weakly temperature dependent, and so considered as constant.

In the El Mously model [27,28], the variation of conductivity obeys a

$$\frac{d\sigma^{-1}}{d\alpha} = \frac{d\sigma}{d\alpha} \quad (9 a)$$

law, which leads to

$$\frac{1}{1 - \alpha_M} = 1 - f_M(t) \quad (9 b)$$

and

$$f_M(t) = \frac{\sigma_c(\sigma_a - \sigma_t)}{\sigma_a(\sigma_c - \sigma_t)} \quad (9 c)$$

The experimental data show an Avrami relation of the form

$$\alpha_M(t) = 1 - \exp(-K_{1,2} \cdot t^{m_{1,2}}) \quad (10)$$

where $K_{1,2}$ and $m_{1,2}$ depend on the temperature and characterize a certain transition defined by the couples (K_1, m_1) .

We ascertain that, although these models lead to a same form of variation for the transformed volume fraction $x(t)$, the physical limits are very different. These divergences are related to the choice of the variations of conductivities

$$\frac{f_M(t)}{f_G(t)} = \frac{\sigma_c(\sigma_a + 2\sigma_t)}{\sigma_a(\sigma_c + 2\sigma_t)} \quad (11)$$

We add that several simple forms for the conductivity [26] lead also to an Avrami relation for $x(t)$. However, all these variations do not present a transition as appears in percolation theory.

Whatever the model considered is, the determination of $x(t)$, which is a macroscopic property, cannot give us any information on the structural properties as the mean number of crystallites of identical volume, at time t .

This will be possible for small values of $x(t)$, e.g. in the case of weak overlapping between the crystallites and where we have

$$\alpha(t) = \alpha_e(t) \quad (12)$$

where $\alpha_e(t)$ is the extended volume fraction.

In Germain's model, the determination of the structural behaviour is erroneous due to the substitution of the real volume fraction $x(t)$ by the extended one (see Table 1 of Ref. 25).

IV. PROPOSED MODEL

The question is now: is it possible to show a possible conjunction between experimental results and theoretical outcomes deduced from percolation theory. The fundamental difference between the nucleation problems (as they have been introduced) and those of the percolation being the growth process, it is interesting to see first the structural behaviour, when the growth is neglected. In fact, when T is close to the glass transition T_g , the growth process can be neglected.

Let us define a predominance rate between the germination and the growth process as:

$$D(T) = \frac{x_g}{x_c} \quad (13)$$

where $x_g(t)$ and $x_c(t)$ are, respectively, the transformed volume ratios, due to germination and growth processes respectively and uniquely.

Let $\tilde{D}(T)$ be the renormalized predominance rate, so that $0 \leq \tilde{D}(T) \leq 1$ for $T_f \geq T \geq T_g$ where T_f is the melting temperature.

Case when $\tilde{D}(T) \rightarrow 1$

The germination process predominates. Let us consider a system of infinite size and volume V_∞ . We divide this medium on identical cells with a volume v_0 for each one. Each cell contains, at least, m_c molecules or atoms as [25]

$$m_c = \left(\frac{2r\sigma}{3\Delta g'} \right)^2 \quad (14)$$

r , σ and $\Delta g'$ are, respectively, a geometrical constant, the Gibb's energy (per unit of area) and the free energy of crystallization.

This relation (14) gives us the critical number of identical entities a cell must contain to give a germ.

Let N_∞ , be the total number of cells within the system

$$N_\infty = \frac{V_\infty}{v_0}$$

When a cell becomes a germ, we look at it as an active centre. Thus, the germination process consists to choose, at random, cells and to convert them into active centres.

The probability p to have an active centre is

$$p = \frac{\text{number of active centres}}{\text{total number of cells}}$$

This is the definition of the transformed volume fraction

$$x = \frac{N v_0}{V_\infty} \quad (15)$$

N is the number of active centres.

The mean number of clusters of size s , is

$$m_s(x) = q_0 s^{-c} \exp \left[-q_1 (x-x_c)^A s^{E_{1,2}} \right] \quad (16)$$

for $s \rightarrow \infty$

x_c is the critical concentration at which the transition occurs. Hence in the strong disorder limit, the percolation results fit perfectly to the structural behaviour of the condensed nucleation systems.

Among these results, we note the singular behaviour of some properties near the percolation threshold x_c , like the conductivity [31,32]

$$[\sigma(x)]_{\text{sing}} \propto (x-x_c)^b \quad (17)$$

where $[\]_{\text{sing}}$ specifies the singular part.

Influence of the growth phenomenon

The ticklish and decisive problem is the influence of the growth on the properties of these systems. When the temperature increases ($T > T_g$), the growth phenomenon becomes important, and we have to find out how we can take it into account.

Once an active centre is born, the growth takes place. In a simple model, this appears like the transformation of the peripheric cells of the germination centres into active cells. So, we must distinguish between the centres activated by the germination process to those activated by the growth process. Although, these centres present the same physical features, their origins are different. When the positions of the activated germs are aleatory distributed, those of the activated growth centres depend on those of the germination. Such a correlation in the spatial distribution of the activated centres suggest to consider the growth as a pseudo-aleatory process.

It has been shown [3] that for pseudo aleatory generation processes, the apparition of the infinite percolation canal is retarded. We assume that this is true for the condensed nucleation systems, and we can use the results of the percolation theory with the following assumptions:

(i) when T increases, the critical concentration x_c increases also, and then the transition is delayed;

(ii) the forms of the variation laws for $n_s(x)$ are not affected. However the growth influence must change internal parameters like $q, \tau, n_{1,2}$ and μ ;

(iii) the background term predominates when T draws near T_f . Thus, for $T \rightarrow T_g$, the transition term predominates, while for $T \rightarrow T_f$, it is the non-transition term which becomes preponderant.

On making an allowance for the last hypothesis, the mean numbers of clusters - s may be expressed as

$$m_s(x) = q_0 s^{-\bar{E}} \exp \left[-q_1 (x-x_c)^{\Delta} s^{\bar{r}_{1,2}} - q_2 s^{\bar{\mu}} \right] \quad (18)$$

where the different coefficient and exponent are temperature dependent.

Temporal variation

Whatever the temperature is, the stochastic process of germination will introduce overlapping between clusters. Their geometrical forms become very irregular and a rigorous study must take account of the variations of the mean radius [17].

For simplification and to obtain a temporal variation of the properties, we suppose on an average, that a crystallite born at time t' will have a volume $v(t,t')$ at time t , as

$$v(t,t') = s' v_0 = a_p (t-t')^{\rho} \quad (19)$$

where s' is the number of active centres, contained in the cluster - s' , a_p and ρ being, respectively, the geometrical constant and the fractal dimensionality. It is clear that all a_p and ρ must depend on the temperature.

Inserting relation (19) into (18), it follows

$$m(t-t', x) = q_0 (t-t')^{-\bar{E}_0} \exp \left\{ -q_1 (x-x_c)^{\Delta} (t-t')^{\bar{r}_{1,2}} - q_2 (t-t')^{\bar{\mu}_0} \right\} \quad (20)$$

where q_0, q_1 and q_2 are constants,

$$\bar{E}_0 = \beta \bar{E}; \quad \bar{r}_{1,2}^0 = \beta \bar{r}_{1,2} \quad \text{and} \quad \bar{\mu}^0 = \beta \bar{\mu}$$

the crystallized volume ratio is written as

$$x(t) = \int m(t-t', x) a_p (t-t')^{\rho} dt' \quad (21)$$

For a given temperature, we distinguish three stages

(i) First stage, when $x < x_c$

$$x(t) = \int A t'^{-\bar{E}} \exp \left\{ -B(x-x_c)^{\Delta} t'^{\bar{r}_1} - C t'^{\bar{\mu}} \right\} dt' \quad (22 a)$$

(ii) Second stage, when $x \approx x_c$

$$x(t) = \int A t'^{-\bar{E}} \exp \left\{ -C t'^{\bar{\mu}} \right\} dt' \quad (22 b)$$

(iii) Third stage, for $x > x_c$

$$x(t) = \int A t'^{-\bar{E}} \exp \left\{ -B(x-x_c)^{\Delta} t'^{\bar{r}_{1,2}} - C t'^{\bar{\mu}} \right\} dt' \quad (22 c)$$

with $A = Q_0$; $B = Q_1$, $C = Q_2$, $\bar{r} = \bar{r}^0 - \rho$; $\bar{n}_{1,2} = n_{1,2}^0$ and $\bar{\mu} = \mu_0$. From these relations and for T close to T_g , the transition term is preponderant, we can write

$$(i) \text{ First stage; } x = \int A t'^{-\bar{r}} \exp \{-B(x-x_c)^{\Delta} t'^{\bar{n}_1}\} dt' \quad (23 a)$$

$$(ii) \text{ Second stage; } x = \int A t'^{-\bar{r}} dt' \quad (23 b)$$

$$(iii) \text{ Third stage; } x = \int A t'^{-\bar{r}} \exp \{-B(x-x_c)^{\Delta} t'^{\bar{n}_2}\} dt' \quad (23 c)$$

and when T is close to T_f , we have

$$x = \int A t'^{-\bar{E}} \exp \left\{ -C t'^{\bar{\mu}} \right\} dt' \quad (23 d)$$

We remark that for $T \rightarrow T_f$, $x_c \rightarrow 1$ and the three regimes mingle to an only one stage.

Comparison with experimental data

The experimental results that we can use, are grounded on measures of conductivities and the $x(t)$ determination. Such a comparison, although still weak, leads to the first confrontation of this model with experiment.

Note that for appropriated parameters, the relations (22) leads to Avrami's variation type for $x(t)$.

A direct calculation, for $T \rightarrow T_g$ gives

$$\alpha(t) = ct - \frac{At^m}{B_1 \bar{r}_{1,2}} \exp \left\{ -B_1 t^{\bar{r}_{1,2}} \right\} \cdot y(t)$$

with

$$y(t) = 1 + \sum_{k=1}^{\infty} \frac{k}{\pi} \frac{(-\bar{z} - \delta \bar{r}_{1,2} + 1) t^{-k \bar{r}_{1,2}}}{B_1^k \cdot \bar{r}_{1,2}^k} \quad (24)$$

and

$$m = -\bar{z} - \bar{r}_{1,2} + 1 \quad ; \quad B_1 = B \cdot (\alpha - \alpha_c)^\Delta$$

For relatively large values of t , and $x \neq x_c$, the summation of equation (24) is very small in front of the unity. If we neglect the variation of the power function in front of the exponential function, we obtain

$$\alpha(t) = 1 - \exp \left\{ -B (\alpha - \alpha_c)^\Delta t^{\bar{r}_{1,2}} \right\} \quad (25)$$

Now, we get a time average for $B(x - x_c)^\Delta$ as

$$\langle B(x - \alpha_c)^\Delta \rangle = \begin{cases} b_1 & \text{for } \alpha < \alpha_c \\ b_2 & \text{for } \alpha > \alpha_c \end{cases} \quad (26)$$

and equation (25) gives

$$\alpha(t) \approx 1 - \exp \left\{ -b_{1,2} t^{\bar{r}_{1,2}} \right\} \quad (27)$$

For $T \rightarrow T_f$ the calculation gives

$$\alpha(t) = ct - \frac{A}{c \bar{\mu}} t^m \exp \left\{ -c t^{\bar{\mu}} \right\} \cdot z(t)$$

and

$$z(t) = 1 + \sum_{k=1}^{\infty} \frac{k}{\pi} \frac{(-\bar{z} - \delta \bar{\mu} + 1) t^{-k \bar{\mu}}}{c^k \cdot \bar{\mu}^k} \quad (28)$$

with

$$m = -\bar{z} - \bar{\mu} + 1$$

the same considerations as before lead to

$$\alpha(t) = 1 - \exp \left\{ -c t^{\bar{\mu}} \right\} \quad (29)$$

The relations (27) and (29) are of Avrami type, and have, respectively, the same form than those given by El Mously and Germain. We specify that here we have not considered the heterogeneous nucleation.

It appears that for $T \rightarrow T_g$ and $T \rightarrow T_f$, the two latter models give asymptotic limits. However the last models do not take in account any transition in the variation of the conductivity.

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