Phase transitions in fractal clusters in the presence of electric fields

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(Received 10 May 2000)

It is shown that if the size distribution of the nuclei formed during phase transition is a fractal cluster, then the spatial distribution of the electric field in the cluster is highly inhomogeneous. Electric field is accumulated in small scales, and its strength grows according to the power law from larger scales to smaller scales. When the dielectric permeability of the nuclei is much larger than that of the surrounding medium, the electric field grows as $E\propto 3^k$, where k is a number of the nucleus in the fractal cluster with the sizes $a_1 \gg a_2 \gg a_3 \gg \cdots \gg a_k$. We determined the work of formation of the nuclei in the fractal cluster taking into account the change of the configuration of electric field E. It is demonstrated that the formation of fractal clusters leads to the dynamics of a phase transition with bifurcations, whereby the growth of a nucleus causes the formation of the new nuclei.

The effect of the electric field on the dynamics of phase transitions is of interest in the analysis of various naturally occurring phenomena, e.g., electric phenomena in the atmosphere, and various technological applications, e.g., electric breakdown of liquid dielectrics. Various aspects of this problem were considered in the literature (see, e.g., Refs. 1 and 2, and references therein). If one neglects the presence of the free charges in the system, i.e., assumes that the spatial density of the free charges is small, the effect of the electric field is proportional to $E^2/8\pi$. The coefficient of proportionality depends upon the geometry of the system and material properties. In the thermodynamical scale, the magnitude of $W_e = (E^2/8\pi)v$, where v is a specific volume per one atom in the nucleus, is rather small. Indeed, a small value $W_e = 10^{-3}-10^{-4}$ K corresponds to a relatively large field $E = 10^5$ V/cm and $v = 10^{-21}-10^{-24}$ cm^3. However, a strong effect of the electric field on the dynamics of phase transitions is observed for considerably smaller fields.[3] There exist also other examples where the effects of electric field and electric current are considerable while the magnitude of this field in a thermodynamic sense is negligibly small.[4–6] Notably, studies reporting the anomalously strong effects of electric fields are not the exception but rather are common. In this connection it is of interest to determine the mechanisms that may cause a considerable increase of the effective W_e in the phenomena which can be affected by electric field.

In this study, we consider the effect of a strong amplification of the field in a fractal cluster due to the renormalization of the geometric coefficient. The physics of this effect is rather simple, and it is associated with the fact that the change of the electric field by the inhomogeneous inclusions is essential in the range of the order of the size of the inclusion. Therefore, if the sizes of the inclusions differ considerably, each inclusion causes an independent distortion of the external field. For certain relative locations of these inclusions, one can attain a considerable amplification of the field. In this Brief Report we considered the simplest situation, and selected a geometry which allows analytical solution. In the framework of this model, the amplification of the electric field $E \sim 3^k$, where k is a number of heterogeneous inclusions in the fractal cluster with the sizes $a_1 \gg a_2 \gg a_3 \gg \cdots \gg a_k$.

The analyzed effect may occur not only for the electric field but also for temperature fields, electric currents, etc. To the best of our knowledge, this effect was not considered previously, at least in the aspect of renormalization of the size of the critical nucleus in a fractal cluster by electric field.

In order to calculate the work of nucleus formation in a polarizable medium W_e caused by the change of the configuration of the electric field, it is necessary to determine the induction of electric field $\mathbf{D}(\mathbf{r})$ and its strength $\mathbf{E}(\mathbf{r})$. In the electrostatic approximation in a locally isotropic medium these functions are determined by the following equations:[7]

$$\nabla \cdot \mathbf{D}(\mathbf{r}) = 0, \quad \mathbf{D} = \varepsilon \mathbf{E}, \quad \nabla \times \mathbf{E} = 0. \tag{1}$$

Boundary conditions for Eqs. (1) imply continuity of the tangential and normal components, E_τ^i and D_n^i, of the electric field at the surface of the ith inclusion and condition at infinity:

$$[E_\tau^i] = 0, \quad [D_n^i] = 0, \quad \mathbf{E}(\mathbf{r}) = \mathbf{E}_0 + O\left(\frac{1}{r}\right)^\beta, \quad r \to \infty, \quad \beta > 1. \tag{2}$$

Consider a cluster consisting of spherical particles with radii a_i, $i = 1,...,k$, and dielectric permittivity ε_1 which is different from the dielectric permittivity of the host medium ε_0. Let $\mathbf{R}_i$ be a radius vector of the center of the ith particle, and assume that the radii of the particles satisfy the following condition:

$$a_i \gg a_{i+1}. \tag{3}$$

The distances between the surfaces of the particles $d_{i,i+1} = |\mathbf{R}_i - \mathbf{R}_{i+1}| - a_i - a_{i+1}$ satisfy the condition

$$a_i \gg d_{i,i+1} \gg a_{i+1}. \tag{4}$$

We will use further that a perturbation caused by a spherical particle with the radius a_i into the configuration of electric field $\mathbf{D}(\mathbf{r})$ is essentially nonzero in the domain $|\mathbf{r}-\mathbf{R}_i|\sim a_i$. For $|\mathbf{r}-\mathbf{R}_i|\gg a_i$, this perturbation can be neglected. Under these conditions the problem can be solved by iterations.

At the first stage a system of equations (1) with boundary conditions (2) is solved for the first particle with a center at $\mathbf{R}_1$ and radius a_1. Then in the space domain where vector $\mathbf{r}$ satisfies simultaneously the conditions

$$|\mathbf{r}-\mathbf{R}_2|\gg a_2, \quad |\mathbf{r}-\mathbf{R}_3|\gg a_3, \ldots, |\mathbf{r}-\mathbf{R}_k|\gg a_k, \tag{5}$$

the expression for $\mathbf{D}(\mathbf{r})$ reads

$$\mathbf{D}(\mathbf{r})=\theta_-\frac{3\varepsilon_1}{\varepsilon_1+2\varepsilon_0}\mathbf{D}_0+\theta_+D_0\left[\mathbf{k}\left(1-\xi(3\mu^2-1)\frac{a_1^3}{|\mathbf{r}-\mathbf{R}_1|^3}\right)-3\mathbf{e}_\perp\xi\mu\sqrt{1-\mu^2}\frac{a_1^3}{|\mathbf{r}-\mathbf{R}_1|^3}\right], \tag{6}$$

where $\theta_-=\theta(-x)$, $\theta_+=\theta(x)$, $x=|\mathbf{r}-\mathbf{R}_1|-a_1$, $\theta(x)$ is a Heaviside function, and

$$\mathbf{D}_0=\varepsilon_0\mathbf{E}_0, \quad \mathbf{k}=\frac{\mathbf{D}_0}{|\mathbf{D}_0|}, \quad \mu=\frac{(\mathbf{r}-\mathbf{R}_1)\cdot\mathbf{k}}{|\mathbf{r}-\mathbf{R}_1|},$$
$$\xi=\frac{\varepsilon_0-\varepsilon_1}{\varepsilon_1+2\varepsilon_0}, \quad \mathbf{e}_\perp=\frac{\mathbf{k}\times[\mathbf{k}\times(\mathbf{r}-R_1)]}{|\mathbf{k}\times(\mathbf{r}-R_1)|}. \tag{7}$$

In order to determine function $\mathbf{D}(\mathbf{r})$ in the domain $|\mathbf{r}-\mathbf{R}_2|\sim a_2$, we must determine a solution of Eqs. (1) with boundary conditions (2) whereby the third of conditions (2) is replaced by

$$\mathbf{E}=\mathbf{E}_0^1+O\left(\frac{a_2}{|\mathbf{r}-\mathbf{R}_2|}\right). \tag{8}$$

According to the condition (4), the second nucleus is located in the domain of influence of the first nucleus. In order to determine $\mathbf{E}_0^1$ and $\mathbf{D}_0^1=\varepsilon_0\mathbf{E}_0^1$, let us rewrite Eq. (6) in the coordinate system with an origin at $\mathbf{R}_2$. Conditions (3) and (4) imply that in the region $|\mathbf{r}-\mathbf{R}_2|\sim d_{12}\ll|\mathbf{R}_2-\mathbf{R}_1|$,

$$|\mathbf{r}-\mathbf{R}_2+\mathbf{R}_2-\mathbf{R}_1|\approx|\mathbf{R}_2-\mathbf{R}_1|\cdot\left(1+\frac{|\mathbf{r}-\mathbf{R}_2|}{|\mathbf{R}_2-\mathbf{R}_1|}\cos\alpha\right)\approx|\mathbf{R}_2-\mathbf{R}_1|,$$

where

$$\cos\alpha=\frac{(\mathbf{r}-\mathbf{R}_2)\cdot(\mathbf{R}_2-\mathbf{R}_1)}{|(\mathbf{r}-\mathbf{R}_2)|\cdot|(\mathbf{R}_2-\mathbf{R}_1)|}.$$

Then Eq. (6) in the region $|\mathbf{r}-\mathbf{R}_2|>a_1$ and $|\mathbf{r}-\mathbf{R}_2|-a_2\sim d_{12}$ can be written as follows:

$$\mathbf{D}=D_0M(\xi,\mu_0)[\mathbf{k}a(\xi,\mu_0)+\mathbf{i}b(\xi,\mu_0)], \tag{9}$$

where

$$M(\xi,\mu_0)=[(\xi+1)^2+3\xi\mu_0^2(\xi-2)]^{1/2},$$

$$a(\xi,\mu_0)=\frac{1-\xi(3\mu_0^2-1)}{M(\xi,\mu_0)},$$

$$b(\xi,\mu_0)=-\frac{3\xi\mu_0\sqrt{1-\mu_0^2}}{M(\xi,\mu_0)}, \quad \mu_0=\frac{\mathbf{k}(\mathbf{R}_2-\mathbf{R}_1)}{|\mathbf{R}_2-\mathbf{R}_1|},$$

$$\mathbf{i}=\frac{\mathbf{k}\times[(\mathbf{R}_2-\mathbf{R}_1)\times\mathbf{k}]}{|(\mathbf{R}_2-\mathbf{R}_1)\times\mathbf{k}|}.$$

Function $M(\xi,\mu_0)$ determines the absolute value of the field while functions a, b, and $a^2+b^2=1$ determine the direction of the field in a set $\mathbf{i}$, $\mathbf{k}$. Parameter ξ varies in the range $-1\leqslant\xi\leqslant\frac{1}{2}$, and function $M(\xi,\mu_0)$ has a maximum at the point $\mu_0=0$ for $0\leqslant\xi\leqslant\frac{1}{2}$. In the range $-1\leqslant\xi\leqslant0$ at $\mu_0=0$, function $M(\xi,\mu_0)$ has a minimum, and it assumes the maximum value in this range at points $\mu_0=\pm1$. Thus if a dielectric permeability of the host medium $\varepsilon_0>\varepsilon_1$, then the maximum of the absolute value of the electric induction is attained in the direction normal to $\mathbf{k}(\mu_0=0)$ and

$$\mathbf{D}\approx\mathbf{D}_0^1=(1+\xi)D_0\mathbf{k}=\frac{3\varepsilon_0}{\varepsilon_1+2\varepsilon_0}D_0\mathbf{k}.$$

If $\varepsilon_0<\varepsilon_1$, or $-1\leqslant\xi\leqslant0$, the maximum of the electric inductance is attained in the direction of $\mathbf{k}$ and

$$\mathbf{D}_0^1=\frac{3\varepsilon_1}{\varepsilon_1+2\varepsilon_0}D_0\mathbf{k}. \tag{10}$$

Hereafter we consider the case (10), especially because the effects of the nuclei are stronger in this case. Thus we have calculated the strength of the electric field $\mathbf{E}_0^1$ in the boundary condition (8), $\mathbf{E}_0^1=\mathbf{D}_0^1/\varepsilon_0$, and we can determine electric induction $\mathbf{D}(\mathbf{r})$ in the vicinity of the nucleus with a radius a_2. The expression for $\mathbf{D}(\mathbf{r})\equiv\mathbf{D}_2$ in the region $|\mathbf{r}-\mathbf{R}_2|\sim a_2$ is obtained directly from Eq. (6) by substituting $a_1,\mathbf{R}_1$ by $a_2,\mathbf{R}_2$ and $\mathbf{D}_0$ by $\mathbf{D}_0^1$, where $\mathbf{D}_0^1$ is given by expression (10). Repeating this procedure, we arrive at the expression for electric induction in the vicinity of the ith nucleus when the nuclei are aligned in the direction $\mathbf{k}$:

$$\mathbf{D}_i(\mathbf{r})=\theta_i^-\left(\frac{3\varepsilon_1}{\varepsilon_1+2\varepsilon_0}\right)^i\mathbf{D}_0+\theta_i^+\left(\frac{3\varepsilon_1}{\varepsilon_1+2\varepsilon_0}\right)^{i-1}\mathbf{D}_0\times\left[\mathbf{k}\left(1-\xi(3\mu_i^2-1)\frac{a_1^3}{|\mathbf{r}-\mathbf{R}_i|^3}\right)-3\overline{e}_\perp\xi\mu_i\sqrt{1-\mu_i^2}\frac{a_i^3}{|\mathbf{r}-\mathbf{R}_i|^3}\right], \tag{11}$$

where θ_i^-, θ_i^+, and μ_i correspond to functions μ, θ_-, and θ_+, where $a_1,\mathbf{R}_1$ are substituted by $a_i,\mathbf{R}_i$.

Now we will determine a work of formation of a fractal cluster of nuclei using a general expression:[7,8]

$$W_e=\int(\mathbf{E}\cdot\mathbf{D}-\mathbf{E}_0\cdot\mathbf{D}_0)dV, \tag{12}$$

where $\mathbf{E}_0$, $\mathbf{D}_0$, and $\mathbf{E},\mathbf{D}$ are the strengths of the electric field and electric induction before and after formation of an inclusion, correspondingly. If a source of the electric field does not change during the formation of a nucleus, W_e can be written as $W_e=\int(\mathbf{E}\cdot\mathbf{D}_0-\mathbf{E}_0\cdot\mathbf{D})dV$. Thus the expression for the work of formation of a cluster W_e^k reads

$$W_e^k=\sum_{i=1}^{k}(\mathbf{E}_i^{\rm in}\cdot\mathbf{D}_{i-1}^{\rm out}-\mathbf{E}_{i-1}^{\rm out}\cdot\mathbf{D}_i^{\rm in})V_i,$$

where V_i is the volume of the ith nucleus.

Note that in the assumed geometry of the fractal, $\mathbf{D}_i^{\rm in}=\varepsilon_1\mathbf{E}_i^{\rm in}$ and $\mathbf{D}_{i-1}^{\rm out}=\varepsilon_0\mathbf{E}_{i-1}^{\rm out}$. Here $\mathbf{D}_i^{\rm in}$ is the value of the electric induction inside the ith nucleus while the electric induction $\mathbf{D}_{i-1}^{\rm out}$ corresponds to the field $\mathbf{D}(\mathbf{r})$ in the domain which is determined by the following two conditions: $|\mathbf{r}-\mathbf{R}_{i-1}|\geqslant a_{i-1}$ and $|\mathbf{r}-\mathbf{R}_i|\geqslant a_i$. The above procedure corresponds to the known procedure for calculating the change of the energy of the field caused by inhomogeneous inclusion (see Ref. 7, Chap. 2, Sec. 11).

Thus we obtain

$$W_e^k=\sum_{i=1}^{k}\tilde{p}_iV_i,\quad \tilde{p}_i=\frac{\varepsilon_0-\varepsilon_1}{8\pi}\left(\frac{3\varepsilon_1}{\varepsilon_1+2\varepsilon_0}\right)^{2i-1}\frac{\varepsilon_0E_0^2}{\varepsilon_1}. \tag{13}$$

Now using the above expression for the work of formation of a fractal cluster W_e^k, we can determine the size of the critical nucleus a_c^i which is required for the ith generation. Parameters of a critical nucleus are determined by the conditions for mechanical and chemical equilibrium in the system.[9,10] Let F be the free energy of the system measured from the free energy of the system prior to the formation of the first nucleus. Using Eq. (13), we can write the following expression for F:

$$F=\sum_{i=1}^{k}f_0(v_i,T)N_i+\alpha S_i+\sum_{i=1}^{k}\tilde{p}_iv_iN_i+f_0(v_0,T)\overline{N}. \tag{14}$$

Here v is a specific volume per atom in the ith nucleus, v_0 is a specific volume per atom of the host phase, S_i is the surface area of the ith nucleus, α is a coefficient of surface tension, $f_0(v_0,T)$ is the free energy per particle without electric field, and $\overline{N}$ is the remaining number of particles of the host phase. The condition for mechanical equilibrium in a system with a volume $V=\Sigma_{i=1}^{k}v_iN_i+v_0\overline{N}$ yields $k+1$ equations:

$$\left(\frac{\partial\Phi}{\partial v_i}\right)_{\{N_i,v_{j\neq i}\}}=\frac{\partial(F+pV)}{\partial v_i}=0,\quad i=0,\dots,k, \tag{15}$$

where $\{\}$ denotes a set of parameters which are kept constant and p is a Lagrange multiplier. It is shown below that p is equal to the thermodynamic pressure in the host phase. Let $\overline{v_0}(p,T)$ and $\overline{v_1}(p,T)$ be solutions of the equation $\partial f_0/\partial v=-p$ for the host phase and the new phase, respectively. Then expressions for the solutions of Eqs. (15) read

$$\begin{aligned} v_i(p,T)&=\overline{v_1}(p+\tilde{p}_i+p_1^s),\quad i=1,\dots,k,\\ v_0(p,T)&=\overline{v_0}(p,T), \end{aligned} \tag{16}$$

where $p_i^s=2\alpha/a_i$ is the pressure of a surface tension in the ith nucleus. Since (see, e.g., Ref. 11) $\mu_\sigma(p,T)=f_0(\overline{v_\sigma}(p,T))+p\overline{v_\sigma}(p,T)$, where σ denotes a particular phase, substituting solutions (16) yields the following expression for the Gibbs potential:

$$\Phi=\sum_{i=1}^{k}\mu_1(p+\tilde{p}_i+p_i^s,T)N_i+\mu_0(p,T)\overline{N}. \tag{17}$$

The condition for chemical equilibrium $\partial\Phi/\partial N_i=0$ yields k equations,

$$\mu_1(p+\tilde{p}_i+p_i^s,T)=\mu_0(p,T), \tag{18}$$

which determine the size of critical nuclei a_i^c for phase transition from phase 0 to phase 1 through the formation of a fractal cluster. Equation (18) allows to determine the relation between the critical nuclei sizes at the $(i-1)$th and ith stages of formation of a fractal cluster provided that the thermodynamic state of the host phase 0 does not change:

$$\frac{2\alpha}{a_i^c}=\frac{2\alpha}{a_{i-1}^c}+\tilde{p}_{i-1}-\tilde{p}_i. \tag{19}$$

In order to estimate the magnitude of the effect, consider a case with a weak oversaturation of phase 0. The size of a critical nucleus of phase 1 without electric field a_0^c is given by the following formula:[11]

$$a_0^c=\frac{2\alpha V_1}{\Delta T\Delta S},$$

where ΔT is the deviation of the temperature from the binodal $T_0(p)$ and $\Delta S=S_1-S_0$ is the difference between specific entropies of the new and the host phases. The domain with a weak oversaturation is defined by the following condition:

$$|\tilde{p}_1|\gg 2\alpha/a_0^c. \tag{20}$$

Linearizing Eq. (18) and taking into account that $|\tilde{p}_i|>|\tilde{p}_{i-1}|$ in the domain determined by condition (20), we find

$$a_i^c=\frac{a_0^c}{1-\dfrac{\tilde{p}_ia_0^c}{2\alpha}}\approx-\frac{2\alpha}{\tilde{p}_i}. \tag{21}$$

Thus at weak oversaturation of a host phase $a_i^c/a_{i-1}^c\sim\tilde{p}_{i-1}/\tilde{p}_i$, and in the case when $\varepsilon_1\gg\varepsilon_0$, $a_i^c/a_{i-1}^c\sim0.1$.

Since a characteristic time of formation of a nucleus[10,12] $\tau\sim\exp(4\pi\alpha a_c^2/3T)$, the rate of the phase transitions increases sharply at each of the successive stages of formation of a fractal cluster.

In this study, we demonstrated that the formation of a fractal heterogeneous cluster may be accompanied by strong renormalization of the field and accumulation of energy in small spatial scales. Clearly such accumulation of energy can cause different phenomena, e.g., electromagnetic radiation, formation of beams of charged particles, heat fluxes, etc. A simple model that we employed in this study was chosen in order to elucidate the possibility for accumulation of strong fields in small spatial scales when the applied external field is relatively small. Strong variation of physical parameters in fractal structures was studied in the past (see, e.g., Refs.

13–16, and references therein). However, most of the theoretical studies of these phenomena were based on the scaling approach and computer simulations. Simple geometry of the fractal cluster used in this study allowed us to solve the considered problem directly and to determine the accumulation of electric field in small scales.

The adopted model of the phase transition is general enough, and it can be refined and used also for the analysis of various other phenomena, e.g., chemical reactions, ionization, etc.

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