Why phantom nuclei must be considered in the Johnson-Mehl-Avrami-Kolmogoroff kinetics

M. Tomellini
Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Roma, Italy

M. Fanfoni
Dipartimento di Fisica, Università di Roma Tor Vergata and Istituto Nazionale di Fisica della Materia, Via della Ricerca Scientifica, 00133 Roma, Italy

(Received 16 December 1996)

In the Johnson-Mehl-Avrami-Kolmogoroff theory, the concepts of phantom nuclei and extended space, which caused not a little confusion among investigators, is an *unavoidable* accident of the theory. A straightforward mathematical derivation of that is presented. Besides, some interesting and important physical consequences related to phantom nuclei have been investigated. [S0163-1829(97)07717-5]

First-order phase transitions implying nucleation and growth are often interpreted on the basis of a phenomenological model known as Johnson-Mehl-Avrami-Kolmogoroff (JMAK) theory.[1–3] Recently, some papers appeared in the literature in which the suitability of employing that model was put under criticism. In particular, it was claimed that to take into account the phantom nucleation leads to an overestimation of the transformed phase.[4] Even though this conclusion has been demonstrated to be incorrect,[5,6] it induced Van Siclen to find a derivation of the JMAK formula bypassing the concept of extended volume and phantom nuclei.[7] Once definitely established that the JMAK formula is correct, the thorough examination and clarification of some conceptual points seem to be necessary so as to better understand the theory and the limits of its applicability.

In this paper we would like to close some gaps that Van Siclen's work leaves open. Particularly, we focus our attention on the unavoidable role played by the so-called "phantom nuclei" in the kinetic expression. For the sake of simplicity, in the following, two-dimensional (2D) phase changes will be considered.

Let us consider an infinite surface where N_0 points per unit area, which play the role of nucleation sites from which a 2D phase transition can start, are marked at random. Furthermore, let us assume the nucleation kinetics

$$\frac{dN}{dt}=N_1\delta(t-z_1)+N_2\delta(t-z_2), \tag{1}$$

δ being Dirac's function, $z_2>z_1$, and $N_0=N_1+N_2$. It goes without saying that both site populations are distributed at random throughout the entire space. The growth law is given in the form $r=r(t-z_i)$ (i=1,2), r being the island radius due to unimpeded growth, t the actual time, and z_i the birth time of the cluster. According to Poisson's distribution at time $t>z_2$, the probability a generical point c will not be transformed is equal to

$$P_0=e^{-(N_1\pi r_1^2+N_2\pi r_2^2)}, \tag{2}$$

where $r_i=r(t-z_i)$ ($t>z_2$). This is also equal to the probability that for $t<z_1$ (i.e., when all nuclei are turned off), the circles centered at c and having radius r_1 and r_2 do not contain any of the N_1 and N_2 marked points, respectively (Fig. 1).[8] The probability that the point c belongs to the transformed phase is

$$S=1-P_0=1-e^{-(N_1\pi r_1^2+N_2\pi r_2^2)}=1-e^{-S_e}, \tag{3}$$

S_e being the "extended" surface.

It can happen that a growing cluster of *type 1* captures one nucleation site of *type 2* before the latter starts growing. Under this circumstances the distance between the type-1 and type-2 nucleation sites is lower than $r(z_2-z_1)$. By definition, such an event can be regarded as the creation of a phantom nucleation site. Let us calculate the probability a phantom cluster be created. Let the generical point c be a nucleation site of type 2. As usual, the probability that at least one point of type 1 lay in a circle of radius $r(z_2-z_1)$, centered at the type-2-selected site is

$$Q_{\text{ph}}=1-e^{-N_1\pi[r(z_2-z_1)]^2}. \tag{4}$$

Incidentally, we note that $Q_{\text{ph}}=S(z_2)$. Equation (4) allows one to evaluate the number density of phantom grains, which is $N_{\text{ph}}=N_2Q_{\text{ph}}$. Thus, once the nucleation law is given for the entire space where the phase transition takes place, phantoms are, *in principle*, unavoidable. To get rid of the phantom clusters, one can attempt to work out the computation of S by considering nucleation occurring only in the uncovered portion of the surface, as actually happens. Nevertheless, as a result of the presence of borders between the two phases, the probability the point c will be transformed depends upon its location on the uncovered surface and, therefore, a single distribution of probability does not exist for all points. The straightforward aforementioned statistical argument cannot be applied any longer.[9] The easiest way to solve the kinetics is to restore the complete randomness of the system by introducing phantoms. As a matter of fact, even in the demonstration proposed in Ref. 7, phantoms have been included in the nucleation rate, because the Poisson distribution has been used.

The very importance of phantoms, in the mathematical expression of the kinetics, is emphasized by the existence of a constraint for the growth law of the clusters. Indeed, it happens that, for peculiar growth laws, a phantom cluster, necessarily of type 2, might overtake the cluster of type 1,

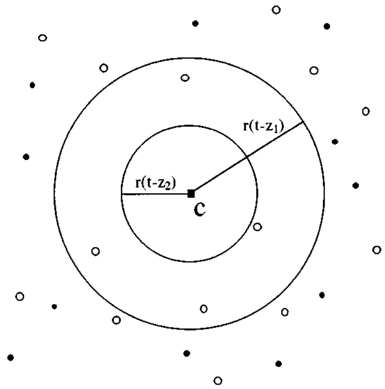

FIG. 1. Configuration for which the c point results untransformed at time $t>z_2$. In fact, no solid symbols (type-1 nuclei) are inside the circle of radius $r(t-z_1)$ and no open symbols (type-2 nuclei) are inside the circle of radius $r(t-z_2)$.

which covers it. For this to occur the growth law must satisfy the condition $\dot{r}(t-z_1)<\dot{r}(t-z_2)$ that is met, for example, by growth laws for which $\partial\dot{r}/\partial t<0$ holds.[10] A kinetics that includes such events cannot be described through the JMAK formula, for the above-reported statistical argument would be no longer applicable. To make the point clearer, let us rewrite Eq. (3) $(t>z_2)$ as

$$S=q_1(1-q_2)+q_2(1-q_1)+q_1q_2, \tag{5}$$

where $q_i=1-e^{-N_i\pi r_i^2}$ $(i=1,2)$ is the probability that at least one of the marked points (type i) falls in a circle, centered at c, of radius r_i. The first two terms [Eq. (5)] are related to cluster configurations where c has been transformed either by type-1 or type-2 clusters, while the last term includes configurations where both type of islands cover c. The second term on the right-hand side of Eq. (5) indicates that point c could be transformed just because of the overgrowth of phantom clusters, that is, because of the ''occurrence'' of unphysical events (Fig. 2). It is worth noting that without the concept of phantom clusters it would have been impossible to find the limit of applicability of the kinetics, as far as the growth law is concerned. A good discussion of this point appeared recently in the literature.[11]

Finally, consider a 2D phase transition in which nucleation does not take place at preexisting nucleation sites. Such a situation is commonly encountered in the formation of thin films on solid surfaces, where clustering of adatoms occurs randomly in the uncovered surface.[12] Again, we assume the actual nucleation rate, per unit surface, to be in the form

$$\frac{dN_a}{dt}=N_{1,a}\delta(t-z_1)+N_{2,a}\delta(t-z_2), \tag{6}$$

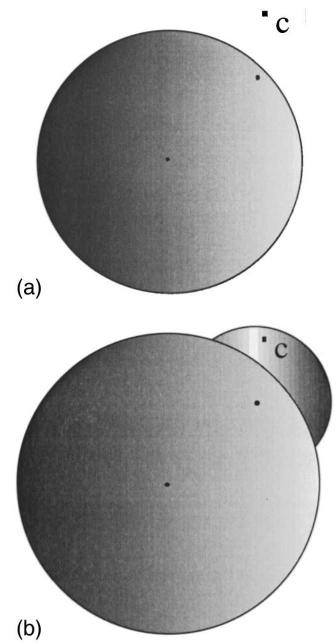

FIG. 2. Overgrowth of a phantom nucleus $(t<z_2)$ (a) can give rise to unphysical events in which the c point results transformed at $t>z_2$ (b).

where $N_{i,a}$ are surface densities and $z_1<z_2$. By definition the $N_{2,a}$ nuclei are distributed at random only on the uncovered surface; consequently, the stationary condition to have a Poisson process is not met. To apply Poisson's distribution the randomness on the whole surface must be restored. In other words, not only has the nucleation to occur in the uncovered surface, but even in the covered portion of the surface at $t=z_2$. This is done by using what one may define a local density of type-2 nuclei at $t=z_2$: $N_{2,a}/[1-S(z_2)]$. Therefore, Eq. (1) becomes

$$\frac{dN}{dt}=N_{1,a}\delta(t-z_1)+\frac{N_{2,a}}{[1-S(z_2)]}\,\delta(t-z_2), \tag{7}$$

with $S(z_1)=0$.

Now we can apply Poisson's probability to obtain the kinetics

$$S=1-\exp\left\{-\pi\left[N_{1,a}r_1^2+\frac{N_{2,a}}{[1-S(z_2)]}\,r_2^2\right]\right\}, \tag{8}$$

where the limit on the growth law, obviously, remains.

In conclusion, we showed that phantom clusters in JMAK kinetics not only are unavoidable, but, as a result of them, the limit of the theory can be easily found.

[1] W. A. Johnson and R. F. Mehl, Trans. Am. Inst. Min. Eng. **135**, 416 (1939).
[2] M. Avrami, J. Chem. Phys. **7**, 1103 (1939); **8**, 212 (1940).
[3] A. N. Kolmogoroff, Izv. Akad. Nauk SSSR, Ser. Matem. **3**, 355 (1937).
[4] V. Erukhimovitch and J. Baram, Phys. Rev. B **50**, 5854 (1994); **51**, 6221 (1995).
[5] V. Sessa, M. Fanfoni, and M. Tomellini, Phys. Rev. B **54**, 836 (1996).
[6] D. Crespo and T. Pradell, Phys. Rev. B **54**, 3101 (1996).

[7] C. DeW. Van Siclen, Phys. Rev. B **54**, 11 845 (1996).
[8] M. Fanfoni and M. Tomellini, Phys. Rev. B **54**, 9828 (1996).
[9] M. Weinberg and R. Kapral, J. Chem. Phys. **91**, 7146 (1989).
[10] For example, in diffusion-controlled growth $r(t,z)\propto\sqrt{t-z}$ and $d\dot{r}/dt\propto-(t-z)^{-3/2}<0$.
[11] P. Uebele and H. Hermann, Model. Simul. Mater. Sci. Eng. **4**, 203 (1996).
[12] See, for instance, M. Zinke-Allmang, L. C. Feldman, and M. H. Grabow, Surf. Sci. Rep. **16**, 377 (1992), and references therein.