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YU.F. ZABASHTA, V.I. KOVALCHUK, L.A. BULAVIN

Taras Shevchenko National University of Kyiv, Faculty of Physics
(64/13, Volodymyrs'ka Str., Kyiv, 01601, Ukraine)

KINETICS OF THE FIRST-ORDER PHASE TRANSITION IN A VARYING TEMPERATURE FIELD

A continual model based on the concepts of the classical theory of phase transformations has been proposed for the first-order phase transition. Using this model, a general formula that relates the relative volume of the initial phase to the temperature varying in the time is obtained. The corresponding formula is also constructed for the case of linear temperature rise. An experimental scheme allowing the fractal dimension and the surface tension of new-phase aggregates to be determined is proposed.

Keywords: first-order phase transition, temperature field, fractal dimension.

1. Introduction

The classical theory of the phase transitions of the first kind [1–3], which was created in the 1930s, continues to be applied in modern researches almost in its original form. The essence of this theory is as follows.

Let phases A and B be in equilibrium at temperatures $T < T_{\mathrm{p}}$, but the transition A $\to$ B takes place at $T > T_{\mathrm{p}}$. As a result of fluctuations, nuclei of phase B appear in phase A. If a nucleus size exceeds a certain critical value, the nucleus begins to grow spontaneously due to the diffusion of particles from the surrounding phase A. The number c of such nuclei formed per unit volume per unit time is determined by the formula

$$c = c_0 \exp\left\{-\frac{\Delta\Phi}{k_{\mathrm{B}}T}\right\}, \tag{1}$$

where $\Delta\Phi$ is the growth of the thermodynamic potential associated with the critical nucleus formation, k_{B} is the Boltzmann constant, and c_0 is a quantity with a weaker dependence on the temperature in comparison with the exponential function, which allows this parameter to be considered constant.

The ratio $\Delta\Phi/(k_{\mathrm{B}}T)$ satisfies the condition

$$\frac{\Delta\Phi}{k_{\mathrm{B}}T} \gg 1. \tag{2}$$

Assuming that the nucleus has a spherical shape, the following formula was obtained for $\Delta\Phi$ [2]:

$$\Delta\Phi = \frac{16\pi}{3}\frac{\sigma^3 T_{\mathrm{p}}^2}{\lambda^2 (T - T_{\mathrm{p}})^2}, \tag{3}$$

where σ is the coefficient of surface tension at the phase interface, and λ is the specific heat of the A $\to$ B transition.

In what follows, the term "nucleus" will be used instead of the term "critical-size nucleus" and the region of phase A larger than the nucleus size will be called the aggregate.

There are two versions of the theory concerned. One of them [1, 2] is based on the assumption that nuclei are removed after their formation, i.e., phase B can exist only in the form of nuclei. The other model [3] considers that the nuclei remain in the system and grow by forming the aggregates. The aggregates are assumed to be spherical. The temperature is considered constant in both cases.

As compared with the aforesaid, there are two differences in the presented article. First, it is assumed that the temperature changes during the phase transition. Second, it is assumed that the aggregates of the new phase can take any shape during their growth.

2. Continual Model of Phase Transition

Since the temperature depends on the time t,

$$T = T(t),$$

then formula (1) with regard for formula (3) can be rewritten in the form

$$c(t) = c_0 \exp\left\{-\frac{16\pi\sigma^3 T_\mathrm{p}^2}{3k_\mathrm{B}\lambda^2(T(t)-T_\mathrm{p})^2 T(t)}\right\}. \tag{4}$$

As a rule, the inequality

$$T - T_\mathrm{p} \ll T_\mathrm{p} \tag{5}$$

holds, which allows the multiplier $1/(k_\mathrm{B}T(t))$ in formula (4) to be approximately substituted by the expression $1/(k_\mathrm{B}T_\mathrm{p})$. Then formula (4) reads

$$c(t) = c_0 \exp\left\{-\frac{M}{(T(t)-T_\mathrm{p})^2}\right\}, \tag{6}$$

where the notation

$$M = \frac{16\pi\sigma^3 T_\mathrm{p}}{3k_\mathrm{B}\lambda^2} \tag{7}$$

was introduced.

The both phases will be considered as continua. We assume that the spatial scale substantially exceeds the size of the nucleus so that the latter can be considered as a point. Suppose that a nucleus is formed at the point Z at the time moment $\tau < t$. Let us introduce a spherical coordinate system (r, ϑ, φ) with the center at this point. We denote the linear growth rate of the nucleus as W.

Generally speaking, the dynamics of nucleus formation is such that the values of W can be different in different directions determined by the coordinate pair (ϑ, φ). For example, it is true, if phase B is anisotropic. However, this feature can be observed for isotropic phase B as well. The matter is that the surface of the nucleus is not smooth on the molecular scale [1, 2]. Accordingly, the conditions for the particles from phase A to attach to different points on the nucleus surface are different. Furthermore, those conditions, generally speaking, can change in the course of nucleus growth. In the framework of the adopted continual model, such complicated circumstances can be taken into account by considering W as a random function of three independent variables: the angles ϑ and φ and the time τ:

$$W = W(\vartheta, \varphi, \tau). \tag{8}$$

Let some point Z_1 have the coordinates $(r_1, \vartheta_1, \varphi_1)$ at the moment of nucleus formation τ. At the time t, this point will belong to the aggregate of phase B growing around the point Z, if

$$r_1 \le \int_\tau^t W(\vartheta_1, \varphi_1, \tau')d\tau'. \tag{9}$$

In other words, the mentioned aggregate will include all points in the volume V bounded by a surface S composed of points located at the distance

$$r_{1S} = \int_\tau^t W(\vartheta_{1S}, \varphi_{1S}, \tau')d\tau' \tag{10}$$

from the coordinate origin. Let the function $W(\vartheta, \varphi, \tau')$ be characterized by the parameter set $Y \equiv \equiv \{y_1, y_2, ..., y_m\}$. As follows from Eq. (10), the volume V must be a function of Y, τ, and t:

$$V = V(Y; \tau, t). \tag{11}$$

Function (8) will be considered invariant with respect to the variable τ'. Then expression (11) takes the form

$$V = V(Y; t - \tau). \tag{12}$$

There is no information about function (8). Therefore, in our opinion, it is reasonable to apply the fractal approach and write expression (12) in the form

$$V(\tau) = a(t-\tau)^\alpha, \tag{13}$$

where α is the scale dimension of the aggregate. In so doing, we accumulate all information about function (8) in the parameters a and α. As one can see from formula (13), the corresponding number of parameters y_i equals two: $y_1 = a$ and $y_2 = \alpha$. These are the parameters that govern the time dependence of the volume V.

For the spherical nucleus, the power exponent $\alpha = 3$ [3]. However, according to experimental data [4–6], the real value is not integer, as a rule. This fact testifies that the aggregate of the new phase has an irregular shape and, accordingly, can be considered as a fractal.

The probability $p(\tau)$ that no nuclei are formed in the volume V in the time interval $(\tau, \tau + \Delta\tau)$ equals

$$p(\tau) = 1 - c(\tau)V(\tau)\Delta\tau. \tag{14}$$

The time will be reckoned from the moment, when the temperature of the heated system becomes equal to T_p. Let us divide the time interval $(0, t)$ into n subintervals with the duration $\Delta\tau = t/n$. By introducing the discrete quantity $\tau_j = j\Delta\tau$ into consideration, we can rewrite expression (14) as follows:

$$p_j = 1 - w_j, \quad w_j = c(j\Delta\tau)V(j\Delta\tau)\Delta\tau. \tag{15}$$

As was done in work [3], the random variables corresponding to different p_j's will be considered as independent quantities. Therefore, the probability q that the point Z_1 will not be included into phase B can be written as the product

$$q = \prod_{j=1}^{n} p_j = \prod_{j=1}^{n}(1 - w_j). \tag{16}$$

Let us take the logarithm of expression (16) and assume that the condition

$$w_j \ll 1 \tag{17}$$

is satisfied. Then, when expanding the result in a power series in w_j, we may confine ourselves to linear terms so that

$$\ln q = -\sum_{j=1}^{n} w_j. \tag{18}$$

Changing the summation in Eq. (18) to the integration, we rewrite this expression in the form

$$\ln q = -\int_0^t c(\tau)V(\tau)d\tau. \tag{19}$$

By its sense, the quantity q is the relative volume θ occupied with phase A at the time moment t, i.e.,

$$\ln\theta = -ac_0 \int_0^t \exp\left\{-\frac{M}{(T(\tau) - T_\mathrm{p})^2}\right\}(t-\tau)^\alpha d\tau. \tag{20}$$

3. Linear Heating Case

When experimentally observing the phase transition in solutions of cellulose derivatives, the most often used heating mode is when the specimen temperature increases linearly in time,

$$T = T_\mathrm{p} + vt. \tag{21}$$

Substituting this expression into formula (20), we obtain

$$\ln\theta = -ac_0 \int_0^t \exp\left\{-\frac{\beta^2}{\tau^2}\right\}(t-\tau)^\alpha d\tau, \tag{22}$$

where the notation

$$\beta^2 = M/v^2 \tag{23}$$

is introduced. Then inequality (2) reads

$$\beta^2/\tau^2 \gg 1. \tag{24}$$

Zeroing the first derivative of the integrand

$$f(\tau) = \exp\left\{-\frac{\beta^2}{\tau^2}\right\}(t-\tau)^\alpha \tag{25}$$

with respect to τ and substituting $\tau = t - \eta$, we find that function (25) has a maximum at

$$\eta = \eta_m = \frac{\alpha t^3}{2\beta^2}, \tag{26}$$

with the maximum height equal to

$$H = \exp\left\{-\frac{\beta^2}{\tau^2}\right\}e^{-\alpha}\eta_m^\alpha. \tag{27}$$

As the maximum width, we take the quantity

$$Q = \eta_2 - \eta_1, \tag{28}$$

where η_2 and η_1 are the values of the variable η at which function (25) equals $H/2$:

$$\exp\left\{-\frac{\beta^2}{(t-\eta_i)^2}\right\}\eta_i^\alpha = \\ = \frac{1}{2}\exp\left\{-\frac{\beta^2}{\tau^2}\right\}e^{-\alpha}\eta_m^\alpha, \quad (i = 1, 2). \tag{29}$$

According to formulas (24) and (26),

$$\eta_m \ll t. \tag{30}$$

By inequality (24), the function $\exp(-\beta^2/\tau^2)$ increases rapidly with τ so that the maximum of function (25) turns out rather sharp. This fact leads to the inequality

$$\eta_i \ll t, \quad (i = 1, 2), \tag{31}$$

which allows us to approximately write

$$(t - \eta_i)^{-2} \approx t^{-2}(1 - 2\eta_i/t). \tag{32}$$

Substituting Eq. (32) into formula (29), we obtain

$$\exp\left\{-\frac{2\beta^2\eta_i}{t^3}\right\}\eta_i^\alpha = \frac{1}{2}\left(\frac{\eta_m}{e}\right)^\alpha. \tag{33}$$

Taking formula (26) into account, this expression can be rewritten in the form

$$\frac{\eta_i}{\eta_m}\exp\left\{-\frac{\eta_i}{\eta_m}\right\} = \frac{2^{-1/\alpha}}{e}. \tag{34}$$

We write η_i as the sum $\eta_i = \eta_m + \Delta\eta_i$. Using the notation $x_i = \Delta\eta_i/\eta_m$, expression (34) looks like

$$(1 + x_i)\exp(-x_i) = 2^{-1/\alpha}. \tag{35}$$

Since $\exp(-x_i) \approx 1 - x_i$, Eq. (35) implies that

$$x_1 = -\sqrt{1 - 2^{-1/\alpha}}, \quad x_2 = \sqrt{1 - 2^{-1/\alpha}}. \tag{36}$$

Hence, the width of the maximum, Q, equals

$$Q = \eta_m(x_2 - x_1) = 2\eta_m\sqrt{1 - 2^{-1/\alpha}}. \tag{37}$$

As τ increases, owing to the rapid growth of the function $\exp(-\beta^2/\tau^2)$, the function $f(\tau)$ has small values, as compared to η_m, outside the maximum concerned. This circumstance allows us to approximately substitute the integral in formula (22) by the area under the maximum, which equals $\eta_m b_m$, and write

$$\ln\theta = -ac_0HQ. \tag{38}$$

From whence, substituting the corresponding values of the relevant quantities, we obtain

$$\ln\theta(T) = -D(T - T_\mathrm{p})^{3(1+\alpha)}\exp\left\{-\frac{M}{(T - T_\mathrm{p})^2}\right\}, \tag{39}$$

where

$$D = 2ac_0e^{-\alpha}\sqrt{1 - 2^{-1/\alpha}}\left[\frac{\alpha}{2vM}\right]^{1+\alpha}. \tag{40}$$

4. Conclusions

The application of any theoretical model in physics is aimed at obtaining information about the structure or physical properties of a studied system. In our case, the parameters containing such information are α, T_p, λ, and σ. Formula (39) explicitly includes the first two of them. The other two quantities in expression (39) – D and M – are certain combinations of the indicated parameters. The availability of the experimentally obtained dependence $\theta(T)$ makes it possible to apply formula (39) in order to determine the numerical values of all four parameters: D, α, T_p, and M.

It is clear that the T_p-value found in such a way will have a much larger error than the T_p-value obtained, for example, using the differential scanning calorimetry (DSC) method. Therefore, when interpreting the experimental dependence $\theta(T)$, it is reasonable to involve the corresponding DSC data, substitute the T_p-value obtained in this way into formula (39), and thus substantially reduce the error in determining the other three parameters: D, α, and M.

As one can see from formula (7), the quantity M is proportional to $\sigma^3T_\mathrm{p}/\lambda^2$. So, in order to determine σ, we must know, besides T_p, the value of λ, which can also be determined in the framework of the DSC method.

Thus, using formula (39 while describing the experimental dependence $\theta(T)$, we can apply the fractal approach and obtain a possibility to determine the scale dimension α of the aggregates of the new phase formed during the phase transition, as well as the coefficient of surface tension σ for them.

As was already mentioned, the application of the fractal approach is required, because the aggregate of a new phase, as a rule, has an arbitrary shape. This is especially true for rigid-chain polymer systems. A typical example of such systems is aqueous solutions of cellulose derivatives. The phase transition in those objects is a subject of intensive research, which opens prospects for novel technologies in various domains, including food industry, personal care production, pharmacology, and construction and environmentally pure materials [7, 8]. The phase separation in such systems is a rather complicated process, and the understanding of its kinetics is necessary to create materials with given physical and chemical properties.

Aqueous solutions of heat-sensitive polymers undergo the sol-gel transition under the heating and return back to the initial state at the subsequent cooling [9, 10]. The gelation in such systems is accompanied by an increase in the solution turbidity, which is a consequence of the phase separation. Currently, the mechanism of gelation has not been studied enough yet despite the existence of a number of relevant hypotheses (see, e.g., works [10–13]). Earlier, we studied the thermally induced change in the macromolecular conformation of cellulose derivatives in highly dilute aqueous solutions [14, 15]. It was shown that the examined sol-gel transition in those systems has a character typical of the phase transition of the first kind. The new phase arising as a result of this transition is a polymer network. A significant rigidity of the chains in this network is responsible for the appearance of fractal aggregates. In our opinion, the fractal dimension of such polymer structures and the corresponding surface tension can be determined using the approach described in this paper. This task will be the aim of our next work.

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Ю.Ф. Забашта, В.І. Ковальчук, Л.А. Булавін

КІНЕТИКА ФАЗОВОГО ПЕРЕХОДУ В ЗМІННОМУ ТЕМПЕРАТУРНОМУ ПОЛІ

Запропоновано континуальну модель фазового переходу першого роду, яка базується на уявленнях класичної теорії фазових перетворень. За допомогою цієї моделі виведено загальну формулу, яка пов'язує відносний об'єм початкової фази із температурою, що змінюється з часом. Відповідну формулу одержано для випадку лінійного зростання температури. Запропоновано схему експерименту, проведення якого дозволяє визначити фрактальну розмірність агрегатів нової фази та поверхневий натяг цих агрегатів.

Ключові слова: фазовий перехід першого роду, температурне поле, фрактальна розмірність.