https://doi.org/10.15407/ujpe67.4.270

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AUTOWAVES INDUCED BY FIRST-ORDER PHASE TRANSITIONS

It has been found that autowaves can emerge at a phase transition of the first order, and their propagation is accompanied by self-oscillations of the temperature and phase composition of the medium. Conditions under which the mentioned waves can appear have been formulated. It has been shown that the propagation of autowaves leads to significant fluctuations of macroscopic parameters in a vicinity of the phase transition temperature.

Keywords: self-oscillations, autowaves, fluctuations, phase transition, self-organization, hydroxypropylmethylcellulose.

1. Introduction

It is well known (see, e.g., [1]) that the specific feature of strongly nonequilibrium systems consists in their ability to self-organize, i.e., to spontaneously form ordered structures, which are conventionally called dissipative. Self-oscillations comprise a dissipative structure that is ordered in time. These are undamped oscillations induced by the action of a nonperiodic energy source. A characteristic feature of self-oscillations is the pressence of a feedback governing the energy production by the nonperiodic source. The dissipative structure ordered in time and space, which is formed due to the propagation of self-oscillations in space, is called an autowave (see, e.g., [1]).

The challenging character of the studies dealing with autowaves is associated, first of all, with the fact that some key processes in the human body – such as the propagation of pulses through nerve fibers, the propagation of excitation in the heart muscle, and so forth – are autowaves. Some processes occurring in non-biological systems, such as combustion, have a similar character.

In this paper, we will show that autowaves can emerge during a phase transition. Earlier, this issue has not been covered in the literature.

2. Formulation of the Problem

Consider the phase transitions $A \leftrightarrow B$, where A is a low-temperature phase and B is a high-temperature one. We will use the thermodynamic approach and consider a physical system undergoing these phase transitions as a continuum.

Let $\phi(\mathbf{r}, t)$ denote a local relative volume occupied by phase B, and $T(\mathbf{r}, t)$ the local temperature, where $\mathbf{r} \equiv \{x, y, z\}$ is the radius vector of any point in the continuum, and t is the time.

The temperature of the system is known (see,e.g., [2]) to substantially affect the kinetics of phase transition. In other words, there is a direct relation be-

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tween the functions $T(\mathbf{r}, t)$ and $\phi(\mathbf{r}, t)$, which is described by a kinetic equation of phase transition. During phase transitions of the first kind, heat is released or absorbed (see, e.g., [2, 3]). Hence, there arises an inverse relation between the functions $\phi(\mathbf{r}, t)$ and $T(\mathbf{r}, t)$. This relation is described by a heat balance equation.

So, we have a system of two equations for two unknown functions $\phi(\mathbf{r}, t)$ and $T(\mathbf{r}, t)$. Our task is to determine the behavior of the solution of this system of equations and show that under certain conditions the function $\phi(\mathbf{r}, t)$ can acquire the form of autowave.

3. Kinetic Equation of Phase Transition

The model of phase transition proposed in work [3] will be used. According to this model, the phase transition takes place owing to the fluctuation-induced formation of spherical nuclei of new phase and their subsequent growth. In [3], for the case when the temperature remains constant during the phase transition, the following kinetic equation was obtained:

$$\phi(t) = \phi_E(t) = 1 - \exp(-\beta t^4), \tag{1}$$

where

$$\beta = C w^3, \tag{2}$$

C is the number of nuclei formed per unit volume per unit time, and w is the linear growth rate.

According to work [2], the temperature dependence of the parameter C is described by the formula

$$C = C_0 \exp\left[-\frac{M}{(T - T_p)^2}\right], \tag{3}$$

where C_0 is a constant, T_p is the phase transition temperature, and the parameter M looks like

$$M = \frac{16\pi}{3}\frac{\sigma^3 T_p^2}{q^2}, \tag{4}$$

where σ is the surface tension coefficient at the interface between the phases, and q is the specific heat of the phase transition.

In work [4], taking formula 3) into account, the following dependence $\phi(\mathbf{r}, t)$ was obtained in the case where the temperature changes during the phase transition:

$$\phi(t) = \phi_T(t) = 1 - \exp\left\{-C_0 w^3 \int\limits_0^t \exp\left[-\frac{M}{(T(\tau) - T_p)^2}\right](t - \tau)^3 d\tau\right\}. \tag{5}$$

Let us assume that the physical system in a definite phase state (A or B) is a set of regions with various ordering degrees. Accordingly, let us introduce the local specific heat of transition $q(\mathbf{r})$. Then the constant M in the kinetic equation (5) transforms into a function $M(\mathbf{r})$, and the function $\phi_T(t)$ into a function $\phi_T(\mathbf{r}, t)$.

4. Heat Balance Equation for a System with Phase Transition

In the general case (see, e.g., [5]), the heat balance equation has the form

$$\dot{Q} = \dot{Q}_i + \dot{Q}_e, \tag{6}$$

where $\dot{Q}$ is the rate of change in the heat amount per unit volume, $\dot{Q}_i$ the amount of heat generated per unit volume per unit time, and $\dot{Q}_e$ the amount of heat entering the unit volume per unit time. The quantity $\dot{Q}_e$ characterizes the internal heat exchange in the physical system.

For the quantity $\dot{Q}$, we have the expression

$$\dot{Q} = \rho c \frac{\partial T}{\partial t}, \tag{7}$$

where ρ is the density and c is the specific heat of the medium. The expression for the summand $\dot{Q}_e$ is

$$\dot{Q}_e = \lambda \Delta T, \tag{8}$$

where λ is the thermal conductivity of the medium, and Δ the Laplacian. The component $\dot{Q}$ is associated with the phase transition and looks like

$$\dot{Q}_i = -\rho q \frac{\partial \phi}{\partial t} \operatorname{sign} \frac{\partial \phi}{\partial t}, \tag{9}$$

where

$$\operatorname{sign} A = \begin{cases} 1 & \text{if } A > 0, \\ -1 & \text{if } A < 0. \end{cases} \tag{10}$$

Substituting Eqs. (7)–(9) into Eq. (6), we obtain

$$\rho c \frac{\partial T}{\partial t} = -\rho q \frac{\partial \phi}{\partial t} \operatorname{sign} \frac{\partial \phi}{\partial t} + \lambda \Delta T. \tag{11}$$

5. Phase Transition in a System with Negligible Internal Heat Exchange

Obtaining an analytical solution of the system of equations (5) and (11) is extremely difficult. Therefore, let us estimate the solution behavior using certain approximations.

Let the ratio

$$\alpha = \frac{\dot{Q}_e}{\dot{Q}_i} \tag{12}$$

satisfy the inequality

$$\alpha \ll 1. \tag{13}$$

Consider the zeroth approximation in the small parameter α. Physically, this approximation corresponds to the neglect of internal heat exchange. Heat exchange is realized via heat fluxes

$$\mathbf{J} = -\lambda \nabla T. \tag{14}$$

In their absence,

$$\nabla T = 0, \tag{15}$$

whence it follows that in the adopted zeroth approximation, the quantity $\mathbf{r}$ can be considered fixed. Accordingly, Eq. (11) reads

$$\frac{dT}{dt} = -\frac{q}{c}\frac{d\phi}{dt}\,\mathrm{sign}\,\frac{d\phi}{dt}. \tag{16}$$

The integral of this equation satisfying the initial conditions

$$T\,(0) = T_0 > T_p, \tag{17}$$

$$\phi\,(0) = 0 \tag{18}$$

looks like

$$T\,(t) = T_0 - \frac{q}{c}\phi_T\,(t)\;\mathrm{sign}\,\frac{d\phi}{dt}. \tag{19}$$

Substituting this expression into relationship (5), we obtain the following integral equation for the function $\phi_T\,(t)$:

$$\phi(t) = \phi_T(t) = 1 - \exp\Bigg\{-C_0 w^3 \times \int_0^t \exp\left[-\frac{M}{\left(T_0 - \frac{q}{c}\phi_T(\tau)\,\mathrm{sign}\,\frac{d\phi_T}{d\tau} - T_p\right)^2}\right] \times (t-\tau)^3 d\tau\Bigg\}. \tag{20}$$

Thus, when describing the phase transition, the zeroth approximation in the small parameter α allows the system of equations (5) and (11) to be replaced by single equation (20).

6. The Mechanism Generating Self-Oscillations During the Phase Transition

Equation (20) will be solved using the step-by-step method. First, let us choose the zeroth approximation. By calculating the derivative

$$\frac{d\phi_T}{dt} = \exp\Bigg\{-C_0 w^3 \times \int_0^t \exp\left[-\frac{M}{\left(T_0 - \frac{q}{c}\phi_T(\tau)\,\mathrm{sign}\,\frac{d\phi_T}{d\tau} - T_p\right)^2}\right] \times (t-\tau)^3 d\tau\Bigg\} C_0 w^3 \times 3\int_0^t \exp\left[-\frac{M}{\left(T_0 - \frac{q}{c}\phi(\tau)\,\mathrm{sign}\,\frac{d\phi_T}{d\tau} - T_p\right)^2}\right](t-\tau)^2 d\tau, \tag{21}$$

we find that

$$\frac{d\phi_T}{dt}\,(0) = 0, \tag{22}$$

$$\frac{d\phi_T}{dt}\,(\infty) = 0. \tag{23}$$

Let the zeroth approximation satisfy Eqs. (22) and (23). The function shown in Fig. 1, *a* does it. It has an inflection point at $t = \eta$. Making the situation simpler, let us change from the function shown in Fig. 1, *a* to a similar function shown in Fig. 1, *b* and consider the latter as the zeroth approximation, i.e.,

$$\phi_0 = \theta\,(t - \eta), \tag{24}$$

where $\theta(t-\eta)$ is the Heaviside unit step function

$$\theta(t-\eta)=\begin{cases}0 & \text{if } t<\eta,\\ 1 & \text{if } t>\eta.\end{cases} \tag{25}$$

For function (1), the inflection point is observed at $t\approx\beta^{-\frac{1}{4}}$. This function has the same behavior as the function shown in Fig. 1, *a*. The same coincidence allows us to write the estimate

$$\eta\approx\beta^{-\frac{1}{4}}. \tag{26}$$

Below, the calculations will be carried out on the basis of the introduced zeroth approximation. Let the inequality

$$T_0-\frac{q}{c}>T_0 \tag{27}$$

hold. According to the selected zeroth approximation (see Fig. 2), the function $\phi_T(t)$ remains equal to zero at $t<\eta$, at the moment $t=\eta$ it jumps to the value $\phi=1$, and at $t>\eta$ remains equal to it. Since there was no phase transition until $t=\eta$, the temperature also does not change (Fig. 2, *b*). At the time moment $t=\eta$, when phase B is formed, heat is absorbed and the temperature drops by a value of q/c. Inequality (27) means that the described events take place within the temperature range of phase B. Hence, the values of the function $T(t)$ and $\phi_T(t)$ remain constant at $t>\eta$. This behavior is described by the formula

$$T(t)=T_0-\frac{q}{c}\theta(t-\eta). \tag{28}$$

The situation changes radically in the case where the inequality

$$T_0-\frac{q}{c}<T_p \tag{29}$$

is obeyed. Now, at the time moment $t=\eta$, when heat is absorbed, the temperature decreases to a value lower than T_p (Fig. 3, *a*). As a result, there appear conditions for the inverse phase transition $B\to A$. In this case, according to the selected zeroth approximation, the function must be equal to unity within the time interval $(\eta,2\eta)$, and afterward decrease in a jump-like manner to zero at the time moment $t=2\eta$ (Fig. 3, *b*). Accordingly, the temperature remains equal to $T_0-\frac{\lambda}{c}$ within the indicated time interval and increases to T_0 at the time moment $t=2\eta$ due

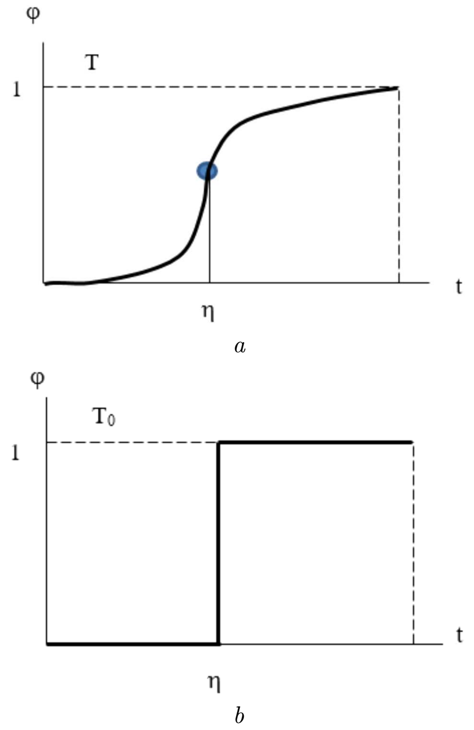


Fig. 1. Zeroth approximation for the functions $\phi(t)$

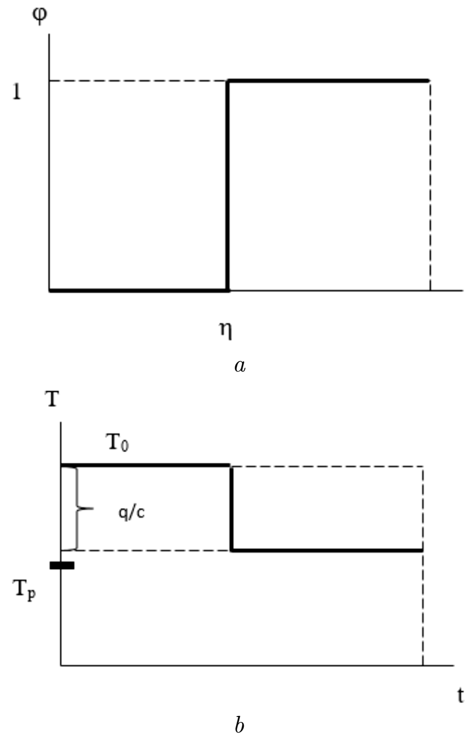
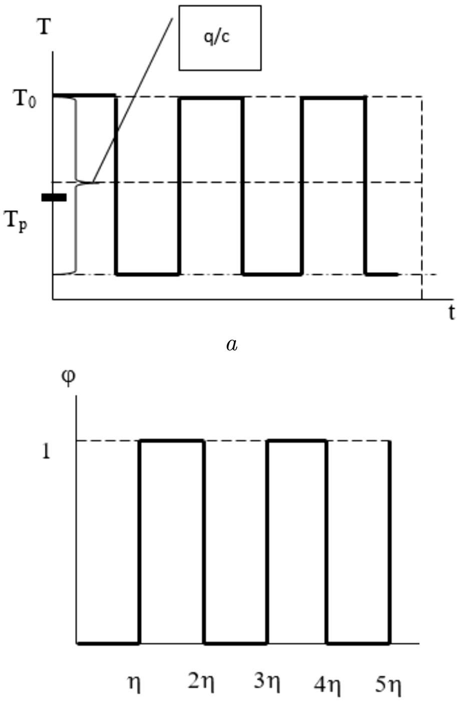


Fig. 2. Non-periodic phase transition mode



a

b

Fig. 3. Periodic phase transition mode

to heat release at the phase transition $B \to A$. Then, the described behavior repeats. In this case, the dependence $T\,(t)$ is a periodic step function of time,

$$\phi_T\,(T) = \sum_k \Big\{ \theta\,[t - k\eta] - \theta\,[t - (k+1)\,\eta] \Big\}$$

$$(k = 1, 3, 5, ..., \infty), \tag{30}$$

$$T(t) = T_0 - \frac{q}{c} \sum_k \Big\{ \theta\,[t - k\eta] - \theta\,[t - (k+1)\,\eta] \Big\}$$

$$(k = 0, 2, 4, ..., \infty). \tag{31}$$

The absence of a periodic energy source and the undamped oscillating behavior of functions (30) and (31) testify that if condition (29) is satisfied, there arise self-oscillations of temperature and phase composition in the system. Their oscillation period equals 2η and they are shifted in time with respect to each other by η. Figures 2 and 3, as well as formulas (30) and (31), correspond to the case when Eqs. (17), (18),and (29) hold.

Now, let the initial conditions be

$$T_0 < T_p, \tag{32}$$

$$\phi\,(0) = 1. \tag{33}$$

Following considerations similar to those that were made when analyzing the behavior of the system for initial conditions (17) and 18), we may assert that self-oscillations are absent in the case

$$T_0 + \frac{q}{c} < T_p, \tag{34}$$

but will arise if

$$T_0 + \frac{q}{c} > T_p. \tag{35}$$

Thus, the appearance of self-oscillations depends on the value of the local specific heat of phase transition. In other words, self-oscillations emerge at those points of the continuum where either of conditions (29) or (35) is satisfied. We will call them the centers of self-oscillations.

7. Autowaves and Thermodynamic Fluctuations Arising During Phase Transition

Consider the first approximation in the small parameter α, thus taking the internal heat exchange into account. In this case, the centers of self-oscillations are transformed into sources of autowaves–pacemakers or leading centers, according to the terminology adopted in work [1]). The duration of the pacemaker action depends on the smallness of the parameter α.

When an autowave propagates, there are self-oscillations of the quantity ϕ at every point of the continuum: one phase alternately transforms into the other. Self-oscillations of the quantity ϕ bring about fluctuations of thermodynamic parameters. One of those parameters is, for example, the local dielectric permittivity $\varepsilon\,(\mathbf{r}, t)$. Pacemakers possess different characteristics, so also different are the frequencies of self-oscillations in the autowaves generated by them. The value of $\varepsilon\,(\mathbf{r}, t)$ is formed owing to the passage of autowaves with various frequencies through the point $\mathbf{r}$. Therefore, the time-dependence of $\varepsilon\,(\mathbf{r}, t)$ is quasi-periodic. For the average value of the dielectric permittivity at the time moment t, we have the formula

$$\varepsilon_a\,(t) = \frac{1}{V} \int\limits_V \varepsilon\,(\mathbf{r}, t) d\mathbf{r}, \tag{36}$$

where V is the volume of the system. For the mean square deviation of the dielectric permittivity, the corresponding expression is

$$\Delta_{\varepsilon}^{2}(t)=\frac{1}{V}\int\limits_{V}\left[\varepsilon(\mathbf{r},t)-\varepsilon_{0}(t)\right]^{2}d\mathbf{r}. \tag{37}$$

The light scattering intensity I is known [6] to be proportional to Δ_{ε}^{2}, i.e.,

$$I(t)\sim\Delta_{\varepsilon}^{2}(t). \tag{38}$$

Since $I(t)$ must have another feature, consider the average scattering intensityI_a, which is defined by the formula

$$I_a=\frac{1}{t_1}\int\limits_{0}^{t_1}I(t)\,dt, \tag{39}$$

where t_1 is the duration of observation.

The temperature T_0 can be identified with the temperature of the thermostat where the test system is arranged. As follows from inequalities (29) and (35), the smaller the quantity $|T_0-T_p|$, the smaller the value of q at which self-oscillations arise. This relation means that if $|T_0-T_p|$ decreases, the number of pacemakers increases, which in turn leads to the growth of I_a. Hence, I_a has to increase as the thermostat temperature approaches the phase transition point.

8. Comparison with Experiment

In work [7], light scattering in the 3% aqueous solution of hydroxypropylmethylcellulose (metholose) in the vicinity of the phase transition temperature was studied. It was found that the dependences $I(t)$ are quasi-periodic in a temperature interval of 303–353 K. It was also found that the value of I_a increases as $|T_0-T_p|$ decreases. Hence, the results obtained [7] confirm the existence of autowaves generated by the first-kind phase transition.

An analysis shows that autowaves arise because of the following reasons. In order to transform a system from the low-temperature phase to the high-temperature one, it is necessary to heat it above the phase transition temperature. This process consumes some heat. A certain amount of high-temperature phase is formed, which is accompanied by heat absorption. Let the system possess low thermal conductivity so that the heat transfer process is slow. In addition, let the system consist of regions with different ordering degrees and, accordingly, different specific heats of phase transition. Under such conditions, in a region with a sufficiently high specific heat of phase transition, due to heat absorption that accompanies the formation of the high-temperature phase, the temperature becomes lower than the phase transition temperature. As a result, the transition from the high-temperature phase to the low-temperature one begins. Now, this transition is accompanied by heat release, i.e., the temperature grows. When it becomes higher than the phase transition temperature, the transition to the high-temperature phase begins again. This process repeats many times. In other words, in this region, there arise self-oscillations of temperature and phase composition. This region becomes a source of autowaves, the propagation of which induces self-oscillations of temperature and phase composition throughout the system.

9. Conclusions

Based on the kinetic equation for the phase transition of the first kind and the heat balance equation, the mechanism of arising temperature and phase self-oscillations has been considered. The autowaves which can arise in the course of the indicated phase transition are considered. It is shown that, under certain conditions during the phase transition, the system can transit into a highly nonequilibrium state and form a dissipative space-time structure, which is a set of autowaves. This model is confirmed by the experimental results [7].

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Received 30.05.22.
Translated from Ukrainian by O.I. Voitenko

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АВТОХВИЛІ, СПРИЧИНЕНІ ФАЗОВИМ ПЕРЕХОДОМ ПЕРШОГО РОДУ

Встановлено, що в процесі фазового переходу першого роду можуть виникати автохвилі, поширення яких супроводжується автоколиваннями температури та фазового складу. Сформульовано умови, за яких згадані хвилі виникають. Показано, що поширення автохвиль має приводити до значних флуктуацій макроскопічних параметрів в околі температури переходу.

Ключові слова: автоколивання, автохвилі, флуктуації, фазовий перехід, самоорганізація, гідроксипропилметилцелюлоза.