THERMAL RELAXATION NEAR PHASE TRANSITIONS

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We consider a phenomenological approach to thermal relaxation processes near phase transitions.

It is known that relaxation effects can significantly influence the propagation of heat in multicomponent, structured materials [1-3]. Near a phase transition these effects can lead to a wide temperature range of the transition and to a dependence on the history of the process.

Since the relaxation processes considered here are accompanied by a rearrangement of the structure and other phase changes, the number of thermodynamic variables characterizing the state of the system increases. In the present paper, we study the case where the phase transition into the isotropic medium is characterized by a single additional parameter η, the order parameter [4]. We let λ be the corresponding affinity to the transition. Then the entropy production due to the change in order is written in the form [5]

$$\sigma = -L\lambda \frac{\partial\eta}{\partial t}, \quad L > 0. \tag{1}$$

From the condition $\sigma \geq 0$ we have in the linear approximation

$$\lambda = -\varepsilon \frac{\partial\eta}{\partial t}, \quad \varepsilon \geqslant 0.$$

The order parameter η is a function of T and λ:

$$\eta = \eta(T, \lambda). \tag{2}$$

Expanding (2) in a power series in λ, in the first approximation we obtain

$$\eta = \eta(T, 0) + \frac{\partial\eta}{\partial\lambda}\lambda. \tag{3}$$

We introduce the notation $\theta = \varepsilon(\partial\eta/\partial\lambda)$, $f(T) = \eta(T, 0)$. Then, with the help of (1),

$$\theta \frac{\partial\eta}{\partial t} + \eta = f(T). \tag{4}$$

From the law of conservation of energy it follows that

$$c \frac{\partial T}{\partial t} + q \frac{\partial\eta}{\partial t} = \nabla(k\nabla T), \tag{5}$$

where $c = (\partial u/\partial T)_\eta$, $q = (\partial u/\partial\eta)_T$, and the coefficients are functions of η.

Therefore, the system of equations (4) and (5) describe the phase transition in the medium.

It is not difficult to see that when $f(T) = e(T - T_0)$ and $\theta \to 0$, we obtain the classical Stefan problem for a phase transition.

As a model we considered the following example, where dimensionless variables are used:

$$c \frac{\partial T}{\partial t} = \mathrm{Fo} \frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right) - q \frac{\partial\eta}{\partial t},$$

$$\theta \frac{\partial\eta}{\partial t} + \eta = e(T),$$

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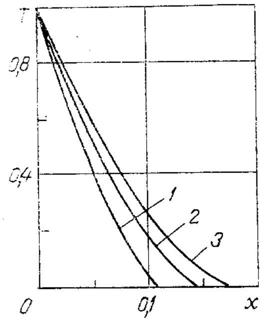

Fig. 1

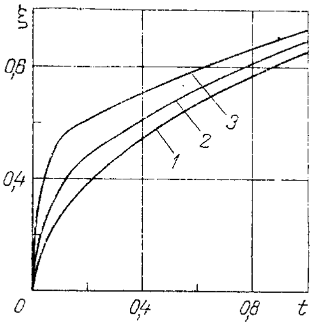

Fig. 2

Fig. 1. Temperature distribution in x: curve 1) θ = 0; 2) 0.05; 3) 0.1.

Fig. 2. Dependence of the motion of the temperature front boundary ξ(t) on time. Curve 1) θ = 0; 2) θ = 0.05; 3) θ = 0.1.

where $c = \frac{c_1}{c_0} + \left(1 - \frac{c_1}{c_0}\right)\eta$; $k = \frac{k_1}{k_0} + \left(1 - \frac{k_1}{k_0}\right)\eta$; $\frac{c_1}{c_0} = 2$; $\frac{k_1}{k_0} = 0.25$; $\mathrm{Fo} = 0.125$; $q = 5$,

and the initial and boundary conditions are $T(x, 0) = \eta(x, 0) = 0$, $T(0, t) = 1$. Here the subscript 0 corresponds to the solid phase ($\eta = 0$) and 1 to the liquid phase ($\eta = 1$).

Calculations were performed for three values of θ. The results for θ = 0.05, θ = 0.1, and the exact solution of the Stefan problem for this case [6] are shown in Figs. 1 and 2. For θ = 0.1 the curves practically coincide with the corresponding curves for θ = 0, i.e., for small values of the parameter θ the solution of (4) and (5) is well-approximated by that of the Stefan problem. Therefore, the solution of (4), (5) at small θ can be considered as equivalent to smoothing the delta function in the solution of the Stefan problem [6].

As already noted, at small θ the effect of the relaxation term in (4) on the process is insignificant. Therefore, in practice, the relaxation term may be ignored in this case. However, relaxation effects are important in determining the parameters of the phase transition, particularly the transition temperature. When θ = 0, the transition occurs instantaneously (a step function). Therefore the transition temperature is the temperature at which one phase transforms into the other. When θ ≠ 0 the transition does not proceed instantaneously. It follows from (4) that the time dependence of the parameter η, characterizing which phase the substance belongs to, has the form

$$\eta = \left[1 - \exp\left(-\frac{t - t_0}{\theta}\right)\right] e(t - t_0)$$

for heating and

$$\eta = 1 - \exp\left(-\frac{t - t_0}{\theta}\right) e(t - t_0)$$

for cooling. Here t_0 is the instant of time when, at an observation point, the temperature has reached the phase transition temperature. Obviously this mechanism gives a change in the state of the material for a certain finite change Δη in the parameter η. In this case the transition will be detected at the instant of time $t_1 = t_0 - \theta \ln(1 - \Delta\eta)$. Then the error in determining the transition temperature will be determined by the change in temperature after time $t_1 - t_0$, which in turn is determined by the rate of change of temperature. In cooling processes the error will have the opposite sign from that in heating processes. These effects may explain the dispersion in the results for the solidification temperatures of petroleum products by different methods.

NOTATION

T, temperature; u, specific internal energy; k, thermal conductivity; Fo, Fourier number; e(·), Heaviside unit step function; T_0, phase transition temperature.

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METHOD OF CONSTRUCTING A SINGLE EQUATION OF STATE SATISFYING THE REQUIREMENTS OF THE SCALING HYPOTHESIS

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We present an equation of state which quantitatively and qualitatively describes correctly the regular part of the thermodynamic surface and also the region near the critical point.

By a single equation of state, we mean a single structural form which within some given small error describes the experimental thermal and caloric data in the gas and liquid phases, and also on the liquid—vapor coexistence curve for temperatures ranging from T_3 up to T_c, and which describes correctly all of the features of the behavior of the material over this temperature range [1].

Among the important features are the following [2]:

1) The limit $\rho \to 0$ and $p \to 0$ (the equation of state of an ideal gas)

$$p(\rho \to 0,\ T) = R\rho T, \tag{1}$$

2) the equality of the chemical potentials on both branches of the liquid—vapor coexistence curve

$$\mu'' - \mu' = 0, \tag{2}$$

3) the Planck—Gibbs rule

$$\left(\frac{dp_n}{dT}\right)_{T=T_c} = \left(\frac{\partial p}{\partial T}\right)_{v=v_c,\,T=T_c}, \tag{3}$$

4) the critical condition

$$\left(\frac{\partial p}{\partial v}\right)_{v=v_c,\,T=T_c} = \left(\frac{\partial^2 p}{\partial v^2}\right)_{v=v_c,\,T=T_c} = 0. \tag{4}$$

In addition to these characteristics it is important to note the singularities of the thermodynamic surface near the critical point. The modern view, based on accurate experimental research and the scaling theory of critical phenomena, holds that the behavior of the

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