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# NONEQUILIBRIUM PHASE BOUNDARIES IN THE EARTH'S MANTLE[1]

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Deep seismic sounding in the earth's mantle has identified radial nonuniformities that are usually interpreted as zones of transition from one phase to another [1]. A widely used technique is the modeling of phase boundaries in terms of strong discontinuities of the properties of the geological medium; at the discontinuity, the standard system of equations is supplemented by the classical Gibbs condition. As a dynamic generalization of the phase equilibrium condition, we and others [2, 3] have derived an equation that relates the difference between the generalized chemical potentials to the dissipation at the discontinuity; the dissipation is predicted from a solution of the problem of the structure of the discontinuity [3, 4]. In the present paper we develop the dynamic model of the transition zone separating coexisting phases [5]. Following published approaches [6-8], we consider the blurred phase boundary with internal dissipation resulting from the nonequilibrium nature of the transition. We demonstrate that correction for the kinetic properties of the phase transition can change our theories of the effect of phase boundaries on the nature of convective flows in the mantle.

1. Divariant transitions can be described by the model of a continuum with internal degrees of freedom [9]. In this case, the variables of the equation for the Gibbs energy of a unit mass $g$ include, beside the pressure $P$ and the temperature $T$, the additional parameters $\xi\{\xi^1,\ldots,\xi^N\}$, which among others may be measures of the chemical and phase composition of a mineral association. The equilibrium values $\xi^*(P,T)$ are determined from the condition that the Gibbs free energy must be minimum, and consequently, $\partial g(P,T,\xi^*)/\partial\xi=0$. Relaxation to the equilibrium state is generally described by the kinetic equation $\dot{\xi}=-\Gamma:\partial g/\partial\xi$ [9], which can be derived phenomenologically from the postulate that the volumetric energy dissipation must be nonnegative $\sigma=-\langle\partial g/\partial\xi\cdot\dot{\xi}\rangle$. Here, $\Gamma$ is a positive definite symmetrical kinetic matrix and the dot designates the full derivative with respect to time. In the case of the special temperature values $T_p(P)$, the global minimum of $g$ is not unique, and we arrive at a case of monovariant transitions, whose equivalents in the earth's mantle are phase boundaries that occur at definite depths. To describe the structure of such boundaries, we must supplement the set of variables that define $g$ by the gradients of $\xi$ [10]. The static phase boundaries in an incompressible medium at fixed pressure and temperature are simulated by nontrivial solutions of the equation $\delta\tilde{g}(\xi,\nabla\xi)/\delta\xi=0$, where $\delta/\delta\xi=\partial/\partial\xi-\nabla_i(\partial/\partial\nabla_i\xi)$ is the variational derivative. In the nonequilibrium case, deriving by analogy the equation for the volume dissipation $\tilde{\sigma}=-\left\langle\frac{\delta\tilde{g}}{\delta\xi}\cdot\dot{\xi}\right\rangle$ [6-8], we arrive at the Ginzburg-Landau kinetic equation:

$$\dot{\xi}=-\Gamma:\delta\tilde{g}/\delta\xi. \tag{1}$$

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To describe nonisothermal transitions in an incompressible medium (at $P$ = const), we must supplement this equation with the balance of entropy

$$\rho_0 T\dot{s} = -\nabla_i q^i + \tilde{\sigma}, \quad \tilde{\sigma} = (\dot{\xi} \cdot \Gamma^{-1} \dot{\xi}), \tag{2}$$

where $\rho_0$ is the constant density, $q^i$ is the heat input vector, and $s$ is the entropy of a unit mass. The closed system of equations (1), (2) was first derived [8] on the basis of heuristic arguments.

To verify Eqs. (1) and (2), we write the first and second laws of thermodynamics for a unit mass [11]:

$$d\tilde{u} = -pd(1/\tilde{\rho}) + dq^{(e)} + dq^{**}, \quad Td\tilde{s} - dq^{(e)} = dq' \geqslant 0, \tag{3}$$

where $\tilde{\rho}dq^{(e)} = -(\nabla_i q^i)\,dt$ is the input of heat, $dq'$ is the uncompensated heat, and $dq^{**}$ is the input of nonthermal energy; in the original derivation [8] it was assumed that $dq^{**} \equiv 0$. Let $\tilde{g} = \tilde{g}(P, T, \xi, \nabla\xi)$; then, $\tilde{s} = -\partial\tilde{g}/\partial T$, $1/\tilde{\rho} = \partial\tilde{g}/\partial P$, $\tilde{u} = \tilde{g} + T\tilde{s} - P/\tilde{\rho}$. Eliminating $dq^{(e)}$ from Eq. (3), we obtain $dq^{**} - dq' - \tilde{s}dT + dP/\tilde{\rho} = d\tilde{g}$, or, by virtue of the noncommutative nature of the operators $d$ and $\nabla$,

$$dq^{**} - dq' = \left[\left\langle \frac{\partial\tilde{g}}{\partial\xi} \cdot \dot{\xi} \right\rangle + \left\langle \frac{\partial\tilde{g}}{\partial\nabla_i\xi} \cdot \nabla_i\dot{\xi} \right\rangle - \left\langle \frac{\partial\tilde{g}}{\partial\nabla_i\xi} \cdot \nabla_j\xi \right\rangle (\nabla_i v^j)\right] dt. \tag{4}$$

Here, $v^i$ is the velocity vector of the medium. Now, assuming [12, 13]

$$\tilde{\rho}dq^{**} = (\nabla_i\tilde{q}^i + \tilde{P}^{ij}\nabla_j v^i)\,dt$$

and making use of the nonnegativity of the dissipation $dq'$, we obtain equations for the tensor of the excess ("reactive") stresses[2] $\tilde{P}^i_j = -\tilde{\rho}\left\langle \frac{\partial\tilde{g}}{\partial\nabla_i\xi} \cdot \nabla_j\xi \right\rangle$ and for the vector of the input of nonthermal energy $\tilde{q}^i = \tilde{\rho}\left\langle \frac{\partial\tilde{g}}{\partial\nabla_i\xi} \cdot \dot{\xi} \right\rangle$; the latter is determined with an error of the order of the solenoidal term. The desired equation for the dissipation $\tilde{\sigma}dt = dq'$ and the kinetic equation can now be derived from Eq. (4) by substituting for $dq^{**}$:

$$\tilde{\sigma} = -\left\langle \left[\frac{\partial\tilde{g}}{\partial\xi} - \frac{1}{\tilde{\rho}}\nabla_i\left(\tilde{\rho}\frac{\partial\tilde{g}}{\partial\nabla_i\xi}\right)\right] \cdot \dot{\xi} \right\rangle \stackrel{\text{def}}{\equiv} -\left\langle \frac{\delta_\rho\tilde{g}}{\delta\xi} \cdot \dot{\xi} \right\rangle; \quad \dot{\xi} = -\Gamma : \frac{\delta_\rho\tilde{g}}{\delta\xi}. \tag{5}$$

For $\tilde{\rho} \equiv \rho_0$, we obtain $\delta_\rho/\delta\xi = \delta/\delta\xi$, and Eq. (5) reduces to (1) and (2).

Let us consider the equilibrium transition. Let $\tau$ be the characteristic time of the process, and let $g_0$ be the energy scale; then $\tau_0 = |\Gamma| \cdot g_0$, the kinetic time parameter. The approximation of infinitely fast kinetics, $\tau/\tau_0 \gg 1$, is similar to the approximation of infinite conductivity in magnetohydrodynamics: we obtain $\delta_\rho\tilde{g}/\delta\xi = 0$, but $\tilde{q}^i(\xi, \nabla\xi, \dot{\xi}) \neq 0$. So as to be specific, we assume that $\xi$ is the degree of completeness of the transition, determined from the condition $1/\rho = \xi/\rho_1 + (1-\xi)/\rho_2$; then, the kinetic equation reduces to an equation of state of the form $P = P(T, \rho, \nabla\rho, \nabla\nabla\rho)$. We have elsewhere discussed a model of the structure of a phase boundary in kinetic equilibrium, described by an equation of state of this type and with dissipation produced by viscous friction [3-5].

2. The postulate that the medium is incompressible and that there is little change in volume in the phase transition enables us to separate the mechanical problem from the kinetic problem and to the consider the case $\tau/\tau_0 \ll 1$. Let $P$ = const, $\rho \equiv \rho_0$, $v^i \equiv 0$; $q_i = -\kappa\nabla_i T$, $\kappa$ is the thermal conductivity. Following published approaches [6-8], we set $\tilde{g} = g(T, \xi) + \frac{1}{2}\cdot\epsilon(\nabla\xi)^2$, where $g$ is a function that is nonconvex in $\xi$ and that in some temperature interval has three extrema, two of which are minima (Fig. 1); $\epsilon > 0$ is a measure of the nonlocal nature of the medium. In contrast to combustion theory, here we may neglect the dependence of the material properties $\Gamma$, $\kappa$ and $\epsilon$ on the temperature. We introduce the dimensionless variables $g/g_0$, $T/T_0$, $t\Gamma_0$, $x\sqrt{\Gamma_0/k_0}$. Here, $\Gamma_0 = \Gamma g_0$, $k_0 = \kappa T_0(\rho_0 g_0)^{-1}$; we also define $\epsilon_0 = \epsilon/g_0$. Retaining the symbols $g$, $T$, $t$ and $x$, we write the basic set of dimensionless equations:

$$\frac{\partial u}{\partial t} = \Delta T + W\Delta\xi\frac{\partial\xi}{\partial t}, \quad \frac{\partial\xi}{\partial t} = -\frac{\partial g}{\partial\xi} + W\Delta\xi. \tag{6}$$

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[2] The generation of surface tension, assumed for regions with large gradients of $\xi$, is due to the nonhydrostatic nature of the stress tensor.

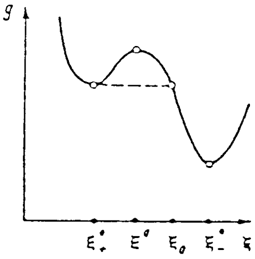


Fig. 1

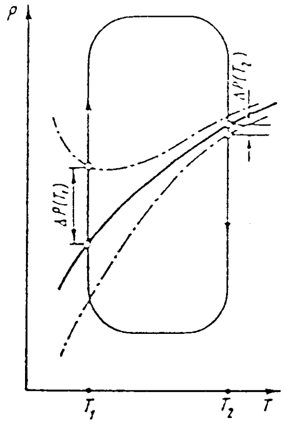


Fig. 2

Fig. 1. Gibbs energy $g$ versus relaxation coordinate $\xi$ at temperature $T = T^*$ at which transition from a metastable phase (+) to a stable phase (-) becomes possible.

Fig. 2. Idealized diagram of a convective cell in $P$-$T$ coordinates. $T_1$ and $T_2$ are temperatures of downward and upward flows. Heavy line is equilibrium curve of monovariant phase transition $T = T_p(P)$. Dashed-dotted lines indicate positions of nonequilibrium phase boundaries in upward and downward flows as a function of flow velocity.

Instead of the entropy balance, we have here the equation for the input of heat: $u = g - T\partial g/\partial T$. The principal dimensionless parameter of the problem, $W = \Gamma_0 \epsilon_0 / k_0$, defines the relationship between the "capillary" length $l_1 = \sqrt{\epsilon_0}$ and the distance that heat can travel during the characteristic time of the reaction, $l_2 = \sqrt{k_0/\Gamma_0}$. The condition $\tau/\tau_0 \ll 1$ obviously represents the case $W \to 0$, and as a result, set (6) exhibits singular perturbation.

We now consider solutions of (6) that contain phase boundaries, i.e., narrow boundary layers with significant variations in $\xi$. We shall model the structure of the phase boundary by a self-similar solution consisting of a traveling wave or kink [6-8]. Introducing the variable $z = x - Dt$, where $D$ is the speed of the discontinuity, we obtain ordinary differential equations for the "external" problem ($W \to 0$):

$$-Du' = T'', \quad -D\xi' = -\partial g/\partial \xi. \tag{7}$$

To define the "internal" asymptotic behavior, we introduce the stretched coordinate $\bar{x} = xW^{-1/2}$. In the zeroth-order approximation with respect to W we obtain

$$\xi'' + \bar{D}\xi' - \partial g/\partial \xi = 0, \quad T'' = 0. \tag{8}$$

The prime denotes the derivative with respect to $z$ in Eq. (7) and with respect to $\bar{z} = \bar{x} - \bar{D}t$ in Eq. (8); and $\bar{D} = DW^{-1/2}$.

We now define a boundary value problem in an infinite region for Eqs. (7): $\xi' \to 0$, $T' \to 0$ for $\bar{z} \to \pm\infty$. It is readily seen that $T(\bar{z}) \equiv T^*$, $\xi(\pm\infty) = \xi_\pm^*$, where $\xi_\pm^*$ are the points at which $g(T^*, \xi)$ has minima; a solution exists in the case of a special value of the parameter $D$. We confine ourselves to the case $D \geqslant 0$, for which a necessary condition is $[g]_-^+ \equiv g(\xi_+^*) - g(\xi_-^*) \geqslant 0$:

$$\sqrt{\frac{W}{2}}\,\frac{g_+ - g_-}{\int_{\xi_+^*}^{\xi_-^*} \sqrt{g - g_-}\,d\xi} \leqslant D \leqslant \sqrt{\frac{W}{2}}\,\frac{g_+ - g_-}{\int_{\xi_+^*}^{\xi_0} \sqrt{g - g_+}\,d\xi}.$$

We denote by $\xi_0$ the root of the equation $g(T^*, \xi) = g(T^*, \xi_+^*)$ lying in the interval $(\xi_+^*, \xi_-^*)$. In $P$-$T$ space, the region in which the solution exists is bounded by the phase equilibrium curve ($g(\xi_+^*) = g(\xi_-^*)$) and the spinoidal line ($\xi_+(P,T) = \xi_0(P,T)$), representing the maximum value of $D$. In the limit of weak nonequilibrium ($\xi_0 \to \xi_-^*$, $g(\xi_+^*) \to g(\xi_-^*)$), the relationship between the thermodynamic "force" $[g]_-^+$ and the flow $D$ becomes linear: $D = \gamma [g]_-^+$, where

$$\gamma = \sqrt{\frac{W}{2}} \left[ \int_{\xi_+^*}^{\xi_-^*} \sqrt{g - g_\pm}\, d\xi \right]^{-1}.$$

Note that $\gamma$ is independent of the details of the extension of the function $g$ into the region $(\xi_+^*, \xi_-^*)$. If $g(T^*, \xi)$ can be approximated by a fourth-order polynomial, then $\partial g/\partial \xi = (\xi - \xi_+^*)(\xi - \xi^0)(\xi - \xi_-^*)$, and Eq. (8) can be integrated, so that the value of $z$ can be calculated exactly for any $[g]_-^+$, i.e.,

$$D = 3\sqrt{W}\, \frac{g(\xi_+^*) - g(\xi_-^*)}{(\xi_-^* - \xi_+^*)^3}. \tag{9}$$

We now analyze the "external" problem, which is also formulated in an infinite region. For Eqs. (7), we must construct a solution that is discontinuous at an internal point (e.g., $z = 0$) and that satisfies the boundary conditions $\xi' \to 0, T' \to 0$ as $z \to \pm\infty$; at the discontinuity, $[T]_-^+ = 0$, $[T']_-^+ = -DQ$., where $Q$ is the heat of the transition. The condition for splicing of the asymptotic expansions is the $T_\pm = T^*$; the quantities $[\xi]_-^+$ and $Q \equiv [u]_-^+ > 0$ are calculated from the solution of the internal problem, e.g.,

$$Q = -T^* \left[ \frac{\partial g}{\partial T} \right]_-^+ + [g]_-^+; \quad [g]_-^+ = \frac{D}{\sqrt{W}} \int_{-\infty}^{\infty} (\xi')^2 dz. \tag{10}$$

The second term on the right side of Eq. (10), describing the heat that is dissipated, is necessary because of the nonequilibrium character of the transition.

Since $D \sim \sqrt{W}$, we can replace the second term of (7) by $\partial g(\xi, T)/\partial \xi = 0$, and hence, $\xi = \xi_p(T)$. The discontinuous solution bounded at infinity is

$$\begin{aligned} &T(z) \equiv T^*, \qquad z \leqslant 0, \\ &-D^{-1} \int_{T^*}^{T} [u^+(\tau, \xi_p^+(\tau)) - u^+(T^*, \xi_p^+(T^*)) + Q]^{-1} d\tau = z, \quad z \geqslant 0. \end{aligned} \tag{11}$$

Linearizing the equation in the neighborhood of $T = T^*, \xi = \xi_+^*$, we obtain

$$\xi_p^+ - \xi_+^* = (T - T^*)(\partial s^+/\partial \xi)^*/(\partial^2 g^+/\partial \xi^2)^*; \; u^+(T, \xi_p^+) = u^+(T^*, \xi_+^*) + c_p^*(T - T^*),$$

where $c_p^*$ is the effective specific heat, and $c_p^* = [\partial u^+/\partial T + T(\partial s^+/\partial \xi)^2/(\partial^2 g^+/\partial \xi^2)]^* > (\partial u^+/\partial T)^* > 0$. Substituting these functions into (11), we arrive at an explicit expression for $T(z)$ at $z > 0$:

$$T(z) = T_0 + (T^* - T_0)\exp(-Dc_p^* z), \quad (T^* - T_0)/T_0 = [s]_-^+/c_p^*.$$

Thus, a thermal boundary layer with a dimensionless thickness of about $(Dc_p^*)^{-1}$ develops in the oncoming flow. Overall, the steady-state solution of the original problem as $W \to 0$ has the form of an adiabatic (but not isentropic) traveling wave of thickness $\sim k_0(\sqrt{\epsilon_0}\,\Gamma_0)^{-1}$ and with an internal isothermal phase discontinuity. The velocity of the wave and the resulting temperature discontinuity are defined by nonequilibrium processes in an isothermal zone of thickness $\sim\sqrt{\epsilon_0} \ll k_0(\Gamma_0\sqrt{\epsilon_0})^{-1}$. The speed of the discontinuity and the state behind it are determined unambiguously from the state ahead of the discontinuity, which is a measure of the degree of metastability that has been attained.

3. As we have shown earlier [1], the effect of phase transitions on thermal convection in the mantle can be reduced to two main factors. So as to deal with a specific case, we consider the exothermic conversion of olivine to a denser phase with the modified spinel structure (depth about 400 km) [1]. The factor that stabilizes the convective instability is the liberation (or absorption) of the heat of the transition in the upward (or downward) flow. A destabilizing effect is produced by horizontal inhomogeneities that result from the fact that the phase transition in the hot ascending flow takes place at a greater depth than that in the cold downward flow. Numerical modeling of finite-amplitude movements [14] indicates that in general, the olivine-spinel transition promotes mantle convection. The conclusion that a destabilizing effect occurs is based on the postulate that the transition is an equilibrium one. Let us use the results obtained above to describe the effect of dissipation in the interphase region on the flow.

A. The Gibbs phase equilibrium condition $[g]_-^+ = 0$, which defines the depth at which the phase boundary occurs, is converted to a dynamic condition for the existence of steady-state solution (9), now with $[g]_-^+ \neq 0$. The degree of displacement of the boundary with pressure increases with the flow velocity. According to Eq. (9), the pressure deviation from the equilibrium value is

$$\Delta p \simeq C \frac{g_0 D}{\Gamma_0 \sqrt{\epsilon_0} [v]^+_-},$$

where $[v]^+_-$ is the volume change produced by the transition, $D$ is the dimensional flow velocity, and $C = -([\xi]^+_-)^3/3 \sim 1$. It is readily seen that the horizontal nonuniformity of position of the phase boundary decreases in exothermic transitions ($dP/dT > 0$) (see Fig. 2) and increases in endothermic transitions ($dP/dT < 0$). In both cases, the nonuniformity has a stabilizing effect. A similar conclusion was reached by Sung and Burns based on a qualitative argument [15].

B. The classical expression for the heat of the transition $Q = T^*[s]^+_-$ is converted in the dynamic case to Eq. (10); in this case, the value of $[g]^+_-$ increases with the flow velocity. Converting to dimensional variables in (9) and (10), we obtain

$$Q = T^*[s]^+_- \left(1 + C \frac{g_0 D}{\Gamma_0 \sqrt{\epsilon_0} T^* [s]^+_-}\right).$$

Since $[g]^+_- > 0$, in exothermic transitions ($[s]^+_- > 0$) the nonequilibrium situation tends to increase the absolute heat of the transition, while the opposite occurs in endothermic transitions ($[s]^+_- < 0$). In both cases, the dissipation has a stabilizing effect on convection.

C. When nonequilibrium processes occur in the interphase region, the steady-state solutions describing penetrating flows exist only in a limited range of values of the properties. For example, an upper bound of the estimate for the flow velocity is about $\Gamma_0 \sqrt{\epsilon_0}$; at faster flow velocities, dissipation produces a blocking effect. This may be the reason for the widely discussed possibility [1, 14] of vertical stratification of the mantle into independently circulating reservoirs. The observed clustering of the maxima of liberated seismic energy near the phase boundaries [15] may be attributed to the unsteady-state character of the penetrative flows, as well as the development and explosive relaxation of unsteady states.

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