

Equilibrium phase interfaces

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Along with adiabatic chemical and phase transitions, which are nonequilibrium and are accompanied by entropy production at the front, it is appropriate to analyze isothermal equilibrium phase transitions. By this we understand the generalization to the dynamic case of the static problem, analyzed by Gibbs,¹ of the equilibrium of continuous phases. Such problems arise, for example, in the description of processes of slow crystallization in a cooling medium.

In the present note we obtain the complete set of conditions at a moving front of an equilibrium phase transition in a heat-conducting, nonlinearly elastic medium. To the usual conditions of continuity of the fluxes of mass, momentum, and energy² we add a relation which is a generalization of the well known condition of continuity of the chemical potential and serves for determining the velocity of the front. The structure of the discontinuity is constructed on the basis of the nonlocal equation of state.

1. Let the phases be characterized by different forms of dependence of the internal-energy function on its arguments (the deformation tensor and entropy). Usually the phase transition is localized in a narrow region of space and can be modeled by the surface of a discontinuity of the characteristics of the medium. The following universal conditions² are valid at the discontinuity:

$$[\rho(D - v_n)]^* = 0 \quad [\rho(D - v_n)v^i + P_k^i n^k]^* = 0 \quad (1)$$

$$[\rho(D - v_n) \left(U + \frac{v^2}{2} \right) + P_k^i n^k v_i]^* = [q^i n_i]^* \quad (2)$$

$$[\rho(D - v_n) S]^* = \left[\frac{q^i n_i}{T} \right]^* + R \quad (3)$$

Here ρ is the density, D is the velocity of the discontinuity, v^i are the components of the velocity vector of the medium, $v^i = v^i n_i$, $v_n = v^i n_i$, n_i are the components of the unit outward (with respect to one of the phases) normal to the discontinuity surface, P_k^i are the components of the deformation tensor, U and S are the specific internal energy and entropy, respectively, $q_i = -\kappa \nabla_i T$ are the components of the heat-flux vector, κ is the coefficient of thermal conductivity, T is the temperature, and R is the entropy production at the discontinuity. The symbol $[f]^*$ denotes the difference between the values of f on each side of the discontinuity surface.

For an equilibrium phase transition we formulate a

model which reduces to the assumptions

$$[T]^* = 0 \quad (4)$$

$$R = 0 \quad (5)$$

The necessity of analyzing additional conditions at the discontinuity is connected with the fact that:

a) The energy equation contains second derivatives of the temperature;

b) to solve the problem one must find the law of motion of the phase interface (a problem with a free boundary).

Eliminating the quantity $[q^i n_i]^*$ from (2) and (3), we obtain

$$[\rho(D - v_n) \left(U - TS + \frac{v^2}{2} \right) + P_k^i n^k v_i]^* = 0 \quad (6)$$

We transform this condition using the Hadamard consistency relation. Let $x^i(\xi^\alpha, t)$ be the law of motion of the medium, where ξ^α are the Lagrangian coordinates, t is the time, and $i = 1, 2, 3$, $\alpha = 1, 2, 3$. Continuity of the functions x^i at the discontinuity gives

$$[x_\alpha^i]^* = \lambda^i n_\alpha, \quad [v^i] = \lambda^i n_4,$$

where

$$x_\alpha^i = \partial x^i / \partial \xi^\alpha, \quad v^i = \frac{\partial x^i}{\partial t}, \quad n_\alpha = x_\alpha^i n_i, \quad n_4 = -(D - v_n)$$

Then for a nonzero mass flux through the phase boundary we obtain from (6) the relation generalizing the condition of continuity of the chemical potential:

$$\left[\left(\frac{v^2}{2} - U + TS \right) \rho n_\alpha + (\rho v_i (D - v_n) + P_k^i n_i) x_\alpha^i \right]^* = 0 \quad (7)$$

It is obvious that only one of the three conditions (7) is independent. In the case of static equilibrium we arrive at the condition

$$[(U - TS) \rho n_\alpha - P_k^i n_i x_\alpha^k]^* = 0,$$

which was obtained in Ref. 3 by the Gibbs method by varying the position of the phase boundary in the Lagrangian coordinates (also see Refs. 4 and 5).

The conditions (1), (2), (4), and (6) comprise a complete set of relations at the phase boundary. The Stefan conditions⁶ for an incompressible medium are obtained

2. Let us consider the problem of the structure of an equilibrium phase boundary. The question of the method of describing the medium within the front is fundamental. First let us discuss the isothermicity condition (4).

If for the external problem we adopt the simplest heat-transfer model, which reduces to the use of the Fourier law, the natural boundary condition at the front for the external problem will be the assignment of the temperature and (independently) the heat flux. It is obvious that if the description of the heat-transfer process in the internal problem is also based on the use of the Fourier law, consistent data will be obtained at the external boundary. In particular, boundary conditions of the type

$$T = T_2, \quad q = q_2,$$

cannot be obtained in this way, since the conditions

$$T \rightarrow T_2, \quad \frac{dT}{dx} \rightarrow -\frac{1}{\kappa} q_2 \quad \text{as} \quad x \rightarrow \pm\infty$$

are incompatible if $q_2 \neq 0$. Therefore, in the analysis of the structure we shall take the quantity q as an independent variable, setting $T = \text{const}$, without singling out the dependences of the heat-flux vector on the other characteristics of the medium and their derivatives of different orders. Here it is implied that we take the limit $\kappa \rightarrow \infty$, $dT/dx \rightarrow 0$, since the heat flux q remains finite.

Let us consider the dimensionless quantity $K = \rho_0 V_0 U_0 L_0 \kappa^{-1} T_0^{-1}$, where ρ_0 , V_0 , U_0 , and T_0 are the characteristic density, velocity, specific internal energy, and temperature, respectively, in the interphase layer, and L_0 is the width of the layer; the quantity K characterizes the ratio of the convective to the conductive heat flux. In view of the smallness of the parameters V_0 and L_0 we can take $K \ll 1$, and this results in a model with "infinite thermal conductivity." We note that the adopted isothermal model agrees with the fundamental assumption (5) of equilibrium.

As is known,² the dissipation connected with heat transfer is written in the form (internal problem)

$$R_T = \int_{-\infty}^{\infty} q \frac{d}{dx} \left(\frac{1}{T} \right) dx$$

Therefore, the condition $T = \text{const}$ results in $R_T = 0$ even for a nonzero heat flux q .

3. According to the general approach developed by L. I. Sedov's school, the model of the medium is assigned if the dependence of the internal- (free-) energy function on its arguments is known, the nonholomic part is isolated in the variational equation,² and the conditions at the discontinuities are assigned. To describe the structure of an equilibrium phase transition in a fluid we use a model medium in which derivatives of the density are introduced into the expression for the free energy.⁷⁻⁹ One can show that the simplest expression has the form^{8,9}

$$F(\rho, \nabla \rho, T) = f(\rho, T) + \epsilon(\rho, T) (\nabla \rho)^2 \quad (8)$$

where ϵ is some positive function which is monotonic in ρ , and f is positive and nonconvex in ρ . For a van der Waals fluid, for example,

Without dwelling on the basis for the expression (8), we note that it describes the natural nonlocal nature (displayed at small distances) of the equation of state.

Using the standard variational procedure,² we obtain the equations for the isothermal, plane, stationary flow of a viscous fluid:

$$\frac{d}{dx} (\rho u) = 0, \quad \frac{d}{dx} \left(P + \rho u^2 - \mu \frac{du}{dx} \right) = 0 \quad (10)$$

where

$$P = \rho^2 \frac{\partial f}{\partial \rho} - \rho^2 \frac{\partial \epsilon}{\partial \rho} \left(\frac{d\rho}{dx} \right)^2 - 2\epsilon \rho^2 \frac{d^2 \rho}{dx^2},$$

u is the velocity, and μ is the coefficient of viscosity.

The energy equation has the form

$$\frac{d}{dx} \left[\rho u \left(U + \frac{P}{\rho} + \frac{u^2}{2} \right) - \mu u \frac{du}{dx} + q \right] = 0, \quad (11)$$

where $U = F - T(\partial F / \partial T)$ is the internal energy and q is the heat flux. Integrating Eq. (10), we obtain

$$\rho^2 \frac{\partial \psi}{\partial \rho} - \rho^2 \frac{\partial \epsilon}{\partial \rho} \left(\frac{d\rho}{dx} \right)^2 - 2\epsilon \rho^2 \frac{d^2 \rho}{dx^2} + \frac{\mu m_0}{\rho^2} \frac{d\rho}{dx} = P_0 \quad (12)$$

where

$$\psi = f - \frac{m_0^2}{2\rho^2}, \quad m_0 = \rho u = \text{const}, \quad P_0 = \text{const}$$

For $\mu = 0$ the system is conservative and Eq. (12) is integrated in quadratures. The solution of interest to us, in the form of a "step," exists for a special choice of the integration constants. For functions $f(\rho, T)$ of the type (9) under consideration one can show that for $|m_0| < M_0$ there exist $P_0 = P_0^*$ and ρ_1 and ρ_2 for which

$$\left(\psi + \frac{P_0^*}{\rho} \right) \Big|_{\rho_1} = \left(\psi + \frac{P_0^*}{\rho} \right) \Big|_{\rho_2}, \quad \frac{\partial}{\partial \rho} \left(\psi + \frac{P_0^*}{\rho} \right) \Big|_{\rho_1, \rho_2} = 0$$

We now obtain the solution of the problem of the structure of the discontinuity by fixing the constant $\mu_0^* = (\psi + P_0^*/\rho)|_{\rho_1}$ in the energy integral. The physical meaning of the quantities P_0^* and μ_0^* becomes obvious if we note that as $x \rightarrow \pm\infty$

$$P + \rho u^2 \rightarrow P_0^*, \quad f + \frac{P}{\rho} + \frac{u^2}{2} \rightarrow \mu_0^*$$

Thus, the following conditions at the discontinuity are obtained for $\mu = 0$:

$$\begin{aligned} [\rho(D - v_n)]_-^+ &= 0, & [P + \rho(D - v_n)^2]_-^+ &= 0, \\ \left[f + \frac{P}{\rho} + \frac{(D - v_n)^2}{2} \right]_-^+ &= 0 \end{aligned} \quad (13)$$

The last of these relations signifies the continuity of the generalized chemical potential at the front; it is equivalent to the condition $R = 0$.

The introduction of dissipation ($\mu \neq 0$) destroys the symmetry of the phases and results in irreversibility of the transition. We rewrite Eq. (12), using the new function $y(\rho) = d\rho/dx$:

$$\frac{\partial}{\partial \rho} \left(\psi + \frac{P_0}{\rho} \right) + \frac{\mu m_0}{\rho^*} y - \frac{\partial \epsilon}{\partial \rho} y^2 - 2\epsilon y \frac{dy}{d\rho} = 0. \quad (14)$$

We can show that for each value of P_0 from the interval (P_{02}, P_{01}) there exist ρ_1 and ρ_2 such that

$$\frac{\partial}{\partial \rho} \left(\psi + \frac{P_0}{\rho} \right) \Big|_{\rho_1, \rho_2} = 0$$

For the first-order equation (14) we set up the boundary conditions $y(\rho_1) = 0$ and $y(\rho_2) = 0$; this permits a unique determination of the value of the parameter $P_0 = P_0^*$ for which a solution exists. In this case, if $\rho(-\infty) = \rho_2$,

$$\left(\psi + \frac{P_0^*}{\rho} \right) \Big|_{\rho_2} - \left(\psi + \frac{P_0^*}{\rho} \right) \Big|_{\rho_1} = \mu m_0 \int_{\rho_1}^{\rho_2} \frac{y d\rho}{\rho^4} = \frac{\mu}{m_0} \int_{-\infty}^{\infty} \left(\frac{du}{dx} \right)^2 dx = \frac{RT}{m_0} \quad (15)$$

In the given case the condition $R = 0$ is not satisfied and it must be replaced by the condition $R = R_0 > 0$, where R_0 is calculated from the solution of the problem of the structure [see (15)]. We note, however, that for $|m_0| \sim o(\sqrt{\tilde{\epsilon}})$, where $\tilde{\epsilon} = \max_{(\rho_1, \rho_2)} \epsilon(\rho)$, we have $R_0 \sim o(1)$ and viscous dissipation can be neglected. Therefore, in the presence of viscosity the condition $R = 0$ is approximate and is applicable for the description of slowly moving boundaries.

4. Let us explain the method of obtaining the solution. The function $g = \psi + P_0/\rho$ with $P_0 \in (P_{02}, P_{01})$ has the form shown in Fig. 1. The equilibrium positions A and C correspond to saddles on the phase plane $(\rho, d\rho/dx)$ while the points B and D correspond to centers ($\mu = 0$) or foci ($\mu \neq 0$). Through the choice of the parameter P_0 one can make sure that a separatrix connecting the two saddles exists. This requires that $g(A) = g(C)$ if $\mu = 0$ and $m_0[g(A) - g(C)] > 0$ if $\mu \neq 0$. We note that in the conservative case with $P_{02} < P_0 < P_0^*$ and with $P_0^* < P_0 < P_{01}$ there will exist soliton solutions corresponding to self-closure of the separatrix of one of the saddles, which for $m_0 = 0$ can be interpreted as a description of the nuclei of a new phase developing in the metastable region. With $P_0 = P_{01}$ and with $P_0 = P_{02}$, however, bifurcation occurs (coalescence of the saddle and the focus B) and the non-trivial solutions drop out. Physically this means that only one phase can exist for the given values of the parameters. A similar bifurcation occurs with an increase in the parameter m_0 , and this allows one to speak only of "slowly" moving fronts ($|m_0| < M_0$). The exact values of the parameters can easily be found in the case of a van der Waals fluid (9). We point out that one cannot continuously be at the point D, although discontinuous transitions

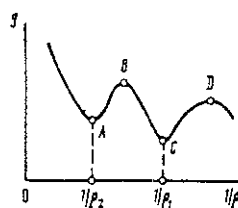


FIG. 1. Characteristic form of the function $g = \psi + P_0/\rho + m_0^2/2\rho^2$ with $|m_0| < M_0$ and $P^* > P_0 > P_{02}$.

of the type C → D, corresponding to the solution of the problem of an isothermal discontinuity in a gas, are possible.

5. As $\tilde{\epsilon} \rightarrow 0$ the continuous solutions obtained converge uniformly to a discontinuous solution. The condition of isothermicity makes it possible to separate the thermal and purely mechanical problems. Thus, Eq. (11) allows one to find the function $q(x)$ from the known function $\rho(x)$. The corresponding condition at a discontinuity has the form

$$[q]^\pm = m_0 \left[U + \frac{P}{\rho} + \frac{(D - v_n)^2}{2} \right]^\pm \quad (16)$$

The condition of continuity of the chemical potential at the front allows us to rewrite (16) in the more usual form $[q]^\pm = \lambda m_0$, where $\lambda = T[S]^\pm$ is the latent heat of the transition. Thus, it is the resultant heat flux which determines the rate of motion of the front (the mass flux). For $[q]^\pm = 0$, we have $m_0 = 0$ and $u = 0$, i.e., we obtain the solution of the problem of the structure of a stationary equilibrium front.⁹

As applications of the relations under consideration we point out the problems of describing the slow ($D \approx$ cm/yr) propagation of the fronts of phase and chemical transformations in the Earth¹⁰ that accompany the heating or cooling of the planet.

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¹J. W. Gibbs. Collected Works, 2 vols. Yale University Press, New Haven (1948).

²L. I. Sedov. A Course in Continuous Mechanics, Vol. 1. 2. Wolters-Noordhoff, Groningen (1971, 1972).

³M. A. Grinfeld. Dokl. Akad. Nauk SSSR 251, 824-827 (1980).

⁴M. A. Grinfeld. Dokl. Akad. Nauk SSSR 253, 567-569 (1981).

⁵M. A. Grinfeld. Lett. Appl. Eng. Sci. 19, 1031-1039 (1981).

⁶H. S. Carslaw and J. C. Jaeger. Conduction of Heat in Solids, 2nd ed. Clarendon Press, Oxford (1959), 510 pp.

⁷M. É. Églit. Prikl. Mat. Mekh. 29, 351-354 (1965).

⁸T. Abraham. Phys. Rep. 53, 93-155 (1979).

⁹J. W. Cahn and J. E. Hilliard. J. Chem. Phys. 28, 258 (1958).

¹⁰L. S. Leibenzon. Izv. Akad. Nauk SSSR. Ser. Geogr. Geofiz. 6, 625-660 (1939).

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