EQUILIBRIUM SHAPE OF A CRYSTAL

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The Gibbs–Curie principle [1, 2] confirms that the external equilibrium shape of a crystal gives the minimum surface energy with a prescribed volume. Here it is implicitly assumed that the main mechanism of mass transfer in forming an equilibrium crystal face is diffusion of substance and vacancies within the crystal; thereby the more widespread mechanism of mass transfer connected with the volume of substance between the crystal and the external medium is excluded. In fact the last mechanism is fundamental in almost all modern technologies for crystal growing from solutions and melts. For this reason it is natural to look at the problem of an equilibrium face from several other positions by studying the problem of the thermodynamic equilibrium of a crystal with its own melt or saturated solution.

The boundary problem is considered below which describes thermodynamic equilibrium of an anisotropic elastic body placed in its own melt. It is shown that it always has a solution. Existence of a solution for this problem is connected with the geometry of phase separation, and for a crystal placed in its own melt, with its external shape. The last situation points to the idea that if in a thermodynamic system of an elastic body–melt it is possible to ignore the surface energy of phase separation, then the equilibrium crystal shape may be determined as that with which a solution of the corresponding problem of thermodynamic equilibrium exists. Some necessary conditions are obtained for existence of a solution for the problem in question which may be assumed to be limits on the equilibrium shape of the crystal face. The result found shows that not only free surface energy is responsible for an equilibrium crystal face. There are other mechanisms connected with conditions for existence of dynamic equilibrium of a crystal with its own melt, with crystal elastic properties, and with the anisotropy of these properties.

1. The first Gibbs principle states that in a state of thermodynamic equilibrium for an isolated system its entropy S reaches a maximum in all possible states of the system with a prescribed energy level, and second that in the state of equilibrium for an isolated system its energy ε reaches a minimum in all possible states of the system with a prescribed entropy level. Gibbs considered them as the main original claims of equilibrium thermodynamics. This only became generally acknowledged recently when it was possible to give an account of all static thermodynamic equilibrium theories by proceeding from them.

The Gibbs principles are considered general. All parameters which may change in the processes in question are essentially subject to variation in them. They are valid in the case when equilibrium is considered for two substances at whose interface it is possible for there to be transformation of one substance into another (phase transition). Here the interface and masses of these substances vary.

Let V be a region in R^3 which is separated into two parts (V_1 and V_2) by surface Ω. Two phases of some substance are in regions V_1 and V_2. The solid phase will be modelled by an elastic body with an internal energy density U_1 depending on distortion x^i_a and entropy s ($x^i_a = \partial x^i/\partial \xi^a$, x^i are Cartesian coordinates of the observer, ξ^a are associated Lagrangian coordinates, indices i, j, k... and a, b, c... take the valeus 1, 2, and 3, the first correspond to projections on axis x^i, the second on axis ξ^a, $x^i = x^i(\xi^a)$ are Cartesian coordinates of particles of the substance in a deformed condition). The second phase is assumed to be liquid. Its internal energy U_2 depends on density ρ and entropy S. If it is accepted that the system in question is adiabatically isolated, then the thermodynamic equilibrium conditions are a stationary point of the energy functional

$$E = \int\limits_{V_1} \rho U_1 \, d\tau + \int\limits_{V_2} \rho U_2 \, d\tau \tag{1.1}$$

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a set of permissible functions $x^i(\xi^a)$, $s(\xi^a)$ which satisfy the adiabatic condition

$$S = \int_{V_1} \rho s \, d\tau + \int_{V_2} \rho s \, d\tau = \mathrm{const} \tag{1.2}$$

($d\tau$ is element of volume).

Euler equations of variation problem (1.1), (1.2) have been obtained in [3]. We give them a geometrically linear variant. We assume displacements of points of the solid phase $w^i(\xi^a) = x^i(\xi^a) - \overset{\circ}{x}{}^i(\xi^a)$ are small, ($\overset{\circ}{x}{}^i(\xi^a)$ are Cartesian coordinates of the points of an elastic body in an undeformed condition). Their gradients are assumed to be small. We assume the elastic body is physically linear:

$$U_1 = U_1(\varepsilon_{ij}, s) = \frac{1}{2} E_0^{ijkl} \varepsilon_{ij} \varepsilon_{kl} + E_0^{ijkl} T_0 \varepsilon_{ij} \alpha_{kl} + C_\varepsilon \exp\left(\frac{s - E_0^{ijkl} \varepsilon_{ij} \alpha_{kl}}{C_\varepsilon} \right).$$

Here $\alpha_{k\ell}$ is thermal expansion coefficient tensor; $\varepsilon_{ij} = (W_{i,j} + w_{j,i})/2$ is strain tensor; a comma in the indices signifies partial differentiation with respect to coordinate; C_ε is heat capacity with constant deformation; $E_0{}^{ijk\ell}$ is elastic isothermal moduli tensor; and T_0 is melting temperature.

The conditions of thermodynamic equilibrium in the elastic body—melt system take the following form: in region V, occupied by solid phase,

$$\sigma^{ij}_{,j} = 0, \sigma^{ij} = \rho \frac{\partial U_1}{\partial \varepsilon_{ij}}, T = \frac{\partial U_1}{\partial s} \tag{1.3}$$

(σ^{ij} is stress tensor in the elastic solid phase, T is temperature); in region V_2 occupied by liquid phase,

$$p_{,i} = 0, \ p = -\rho^2 \frac{\partial U_2}{\partial \rho}, \ T = \frac{\partial U_2}{\partial s} \tag{1.4}$$

(p is pressure in the melt). In addition, at Ω there should be fulfillment of the condition of equality for mechanical forces

$$\sigma^{ij} n_j - p n^i |_\Omega = 0 \tag{1.5}$$

and thermodynamic potentials

$$(\mu^i_{1j} - \mu^i_{2j}) n_i |_\Omega = 0 \tag{1.6}$$

(n_i are vector components of the normal to Ω). Thermodynamic potentials for the solid and liquid phases have the form

$$\mu^i_{1j} = -\sigma^{ik} \varepsilon_{kj} + \overset{\circ}{\rho}_1 (U_1 - Ts) \delta^i_j, \ \mu^i_{2j} = \overset{\circ}{\rho}_2 \left(\frac{p}{\rho} + U_2 - Ts \right) \delta^i_j, \tag{1.7}$$

where $\overset{\circ}{\rho}_1$, $\overset{\circ}{\rho}_2$ are densities of the solid and liquid phases in the undeformed condition and δ^i_j is the Kronecker symbol. As shown in [3], among three conditions of (1.6) only one is independent. It is possible to separate it by turning (1.6), for example, with the vector of normal n_i. The relationships (1.6) taking account of (1.7) are presented as

$$-\sigma^{ik} \varepsilon_{kj} n_i n^j + \overset{\circ}{\rho}_1 (U_1 - Ts_1) |_\Omega = \overset{\circ}{\rho}_2 \left(\frac{p}{\rho} + U_2 - Ts_2 \right) \Big|_\Omega.$$

2. We show that problem (1.3)-(1.6) does not always have a solution. For this purpose we shall assume that the solid phase is uniform but anisotropic. We assume that $V_1 \subset V_2$. This corresponds to the situation when an elastic anisotropic body is in its own melt. We also assume that the melt is hydrostatically compressed:

$$p |_{\partial V_2} = p_0. \tag{2.1}$$

In the general case temperature T is a Lagrangian factor in variation problem (1.1), (1.2) for limiting (1.2), and consequently T is a real number. This means that in thermodynamic equilibrium in the solid—melt system the temperature is constant (T = const). The first equation of (1.4) and boundary condition (2.1) lead to the situation that if a solution of the original problem exists, then pressure in the melt $p = p_0$. From the fact that in region V_2 temperature and pressure are constant, there follows uniformly through space in region V_2 and $s = s_2 = \text{const}$. This reflects the generally known fact that a molten heat conducting material may be in thermodynamic equiilbrium only with constant fundamental parameters throughout the volume.

It is easy to prove that spherical tensor $\sigma^{ij} = -p_0\delta^{ij}$ and $s = s_1 = \text{const}$ satisfy Eqs. (1.3) in region V, occupied by solid phase, and boundary condition (1.5). It is noted that in view of linearity of the elastic problem in region V, the solution obtained is unique. Whence uniqueness follows for the solution constructed for region V_2.

In order that the solutions of Eqs. (1.3) and (1.4) in regions V_1 and V_2 constructed give a solution of the original problem for thermodynamic equilibrium in the solid—melt system it is necessary to satisfy relationship (1.6). We analyze it. It is evident that the right-hand part of it is a value constant in Ω. The left-hand part is presented in the form

$$-\sigma^{ik}\varepsilon_{kj}n_i n^j + \overset{\circ}{\rho}_1(U_1 - Ts_1) = E_k^{ijk} n_i n_j p_0^2 + \overset{\circ}{\rho}_1(U_1 - Ts_1), \qquad (2.2)$$

where $E^{ijk\ell}$ is tensor of elastic adiabatic material compliances. Then the required condition for fulfillment of condition (1.6) in Ω is constancy of the right-hand part of (2.2) in Ω. The second term of (2.2) satisfies this requirement, which follows from the solution of Eq. (1.3) constructed for the solid phase. The first term of (2.2) is not independent of spatial coordinates. This is connected with the fact that vector components of the normal depend on x. In particular, if Ω is a sphere, then the first term of (2.2) at different points on the sphere takes different values in the general case, and consequently it depends on spatial coordinates. Thereby it is possible to confirm the problem of thermodynamic equilibrium of an anisotropic sphere in its own melt which is hydrostatically compressed does not have a solution.

Thus, a necessary condition for existence of a solution to the problem of thermodynamic equilibrium for an elastic anisotropic body with its hydrostatically compressed melt is the condition

$$E_k^{ijk} n_i n_j |_{\Omega} = \text{const}, \qquad (2.3)$$

and it is possible to consider it as a limitation on the shape of the interface with which solution of the problem of thermodynamic equilibrium exists.

Comments. 1. It is logical that in studying an equilibrium face of a crystal in a thermodynamic elastic body—melt system it is necessary to introduce one element, i.e., an interface, ascribing to it some free surface energy. This is equivalent to the fact that to functionals for total energy and entropy it is necessary to add corresponding surface integrals. However, if the density of free surface energy is of the order of the density of phase energy, additions for macrobodies may evidently be ignored since surface energy in this case will be of the order of $\delta/L \ll 1$ compared with the phase energy (δ is interphase layer thickness, L is characteristic size of the system).

2. For isotropic elastic materials (2.3) is satisfied identically. In fact, $E^{ijk\ell}$ here has the structure $E^{ijk\ell} = A\delta^{ij}\delta^{k\ell} + B\delta^{ik}\delta^{j\ell}$, where A and B are material constants. Whence

$$E_{ijk}^{k} n^i n^j = (3A + B) n_i n^i = 3A + B = \text{const}.$$

3. In the general case solutions of Eq. (2.3) are second order plane surfaces. This is confirmed in experiments [4] where an equilibrium face is a series of flat surfaces which do not intersect along a straight line, but are connected by rounded sections. The Wolf theorem ignores this fact from the start by not permitting any other forms of face apart from flat. Nonetheless, Landau on the basis of the Wolf theorem explained the existence of these "rounded" areas [5]. For this he studied in some detail some topological properties of free energy functions for a crystallographic plane in relation to its orientation.

4. Similar to (2.3) the structure has a necessary condition for existence of a solution to the problem of thermodynamic equilibrium of a system consisting of two uniform solid phases of a single material:

$$\left(E'^{k}_{ijk} - E''^{k}_{ijk}\right) n^i n^j \Big|_{\Omega} = \mathrm{const}$$

($E'_{ijk\ell}$ and $E''_{ijk\ell}$ are elastic adiabatic compliance tensors for the corresponding phases). It also follows from this that the interface may be plane or a second order surface.

5. The result obtained is also of practical interest. It is well-known [6] that directionally solidified eutectic alloys from a phenomenological point of view are anisotropic materials. In order to obtain in them a regular columnar or lamellar structure it is very important to have control of the shape of the interface with direction solidification. For very slow, almost equilibrium processes of directional solidification, an increase in pressure in the system leads to the situation that the phase interface will tend towards a flat surface or to a second order surface. Practice shows that in fact a plane boundary gives the best regular eutectic alloy structure.

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