A variational principle is formulated for a two-phase nonequilibrium system; under certain conditions, this principle is equivalent to balance equations within the phases and on the moving boundary.

In [1], a variational principle was considered for the case of heat and mass transfer in a two-phase system with moving interface under the assumption that there are no surface sources. Later [2], on the basis of stochastic ideas, a variational principle was formulated in a more general form and the conditions of variation were justified. In the present paper, this principle will be applied to the case of a flat moving boundary of finite width.

It was assumed in [2] that the system is of a single phase and that the F parameters [2, 3] are specified on the boundary of its four-region. We now suppose that a thermodynamic system within which the F parameters are continuous consists of two subsystems (phases) separated by a third subsystem, which we shall call the boundary or boundary layer. We assume that the boundary has a thickness which is not zero but is still fairly small. We assume that on the transition from one side f' of the boundary to its other side f" the F parameters change from F' to F".

The Lagrange function is

\[ L = \int \mathcal{L} d\mathcal{V} = \sum_{\alpha} \int_\mathcal{V}_\alpha \mathcal{L} d\mathcal{V} + \int_{\mathcal{V}_b} \mathcal{L} d\mathcal{V}, \]  

where \( \mathcal{V}, \mathcal{V}_\alpha, \) and \( \mathcal{V}_b \) are, respectively, the volume of the complete system, subsystem \( \alpha \), and the boundary, respectively. In the laboratory frame [2]

\[ \mathcal{L} = \Lambda (C, F, \partial F / \partial t, \nabla F) = \int \mathcal{L} d\mathcal{V} + \rho \partial \Phi / \partial t + \epsilon \mathcal{F}, \]  

The index 0 identifies quantities referring to the set of C parameters, which are constant with respect to the variation. We assume that within the volume of the boundary

\( \mathbf{F}_i = \mathbf{F}_i^1 + \Delta \mathbf{F}_i^1 \). Then the density of the Lagrange function of the boundary can be written in the form

\[
\Lambda = I_i \nabla \mathbf{F}_i + \rho_i (\partial \mathbf{F}_i / \partial t) + \rho_i (\partial \mathbf{F}_i / \partial t) + F_i \mathbf{v}_i + \Delta \mathbf{F}_i. \tag{3}
\]

The variational equation

\[
\int_I \mathbf{L} \, dt = 0
\]

can be reduced, using (1) and (3), to the form

\[
\int_I \left\{ \sum_{i=1}^n \left( \int_{f_i} (\partial \mathbf{A}_i / \partial \mathbf{F}_i) \partial \mathbf{F}_i + \int_{f_i} \Lambda \delta \mathbf{r}_i \, d\mathbf{f} \right) + \int_{f_i} (\partial \mathbf{A}_i / \partial \mathbf{V}_i) \partial \mathbf{F}_i \partial \mathbf{V}_i + \int_{f_i} \Lambda \delta \mathbf{r}_i \, d\mathbf{f} \right\} dt = 0, \tag{4}
\]

where \( f_i \) and \( f \) are, respectively, the surface which separates subsystem \( \alpha \) from the boundary and the surface surrounding the boundary; \( \mathbf{r}_i \) is the vector which determines the position of the boundary in the laboratory frame. The integrals over the outer surface of the system are omitted, because the \( F \) parameters on this surface are assumed to be given (or the fluxes to vanish). Also omitted are the integrals with variations of the \( F \) parameters at the initial and final times.

We have

\[
\int_{f_i} (\partial \mathbf{A}_i / \partial \mathbf{F}_i) \partial \mathbf{F}_i \, d\mathbf{f} = \int_{f_i} (\partial \mathbf{A}_i / \partial \mathbf{V}_i) \partial \mathbf{F}_i \, d\mathbf{f} = \int_{f_i} \Lambda \delta \mathbf{r}_i \, d\mathbf{f},
\]

because the quantities \( \Delta \mathbf{F}_i \) vanish on the surface \( f' \). Here, \( \Delta \mathbf{F}_i = \mathbf{F}_i^1 - \mathbf{F}_i^1 \).

The volume element \( dV \) of the surface layer can be chosen in the form \( dV = \mathbf{n} \, dA \), where \( \mathbf{n} \) is the direction of the axis perpendicular to the surface \( f' \) and directed from the first subsystem. We have

\[
\int_{f_i} \delta \mathbf{F}_i \, d\mathbf{r}_i \cdot dV = \int_{f_i} \delta \mathbf{F}_i \, d\mathbf{n} \, dA = \int_{f_i} \delta \mathbf{F}_i \, dA = \int_{f_i} \delta \mathbf{F}_i \, dA = \int_{f_i} \mathbf{n} \, d\mathbf{n} \, dA - (\mathbf{V}_i - \mathbf{V}_f) \, dA.
\]

The integral \( \int_{f_i} \delta \mathbf{r}_i \, d\mathbf{n} \) expresses the amount of substance \( i \) per unit area of the surface \( f' \). In addition, we introduce the notation \( \sigma_i = \int_{f_i} \mathbf{n} \, d\mathbf{n} \). We assume that the surfaces \( f' \) and \( f'' \) are so close that one can assume

\[
\int_{f_i} \delta \mathbf{F}_i \, d\mathbf{f} = - \int_{f_i} \delta \mathbf{F}_i \, d\mathbf{f}, \quad \mathbf{V}_f = \mathbf{V}_i.
\]

The sum of the integrals containing the variation \( \delta \mathbf{r}_i \) of the position of the surface surrounding the surface layer is zero.

If we assume further that the variations of the \( F \) parameters within the subsystems and the surface layer and on the surfaces \( f' \) and \( f'' \) are independent, then we obtain, respectively, for points within the subsystems and for the surface layer the equations

\[
\delta \mathbf{A}_i / \partial \mathbf{F}_i = 0, \quad \delta \mathbf{A}_i / \partial \mathbf{F}_i = 0 \tag{5}
\]

and, if the amount of substance \( i \) in the boundary layer is unchanged, the boundary conditions

\[
\partial \mathbf{A}_i / \partial \mathbf{V}_i = \partial \mathbf{A}_i / \partial \mathbf{V}_i + (\mathbf{v}_i - \mathbf{v}_f) \, \mathbf{n}_i, \tag{6}
\]

\[
\partial \mathbf{A}_i / \partial \mathbf{V}_i = (\partial \mathbf{A}_i / \partial \mathbf{V}_i)'. \tag{7}
\]

We substitute (2) and (3), respectively, in (6) and (7), and then

\[
\mathbf{I}_i = \mathbf{I}_i + (\mathbf{v}_i - \mathbf{v}_f) \, \mathbf{n}_i, \tag{8}
\]

\[
\mathbf{I}_i = \mathbf{I}_i. \tag{9}
\]

Here, \( \mathbf{I}_i \) and \( \mathbf{I}_i' \) are the fluxes in the neighborhood of the surfaces \( f' \) and \( f'' \) from the side of the first and the second phase, respectively; \( I_{i f} \) is the flux in the boundary layer in