THE SHAPE AND VELOCITY OF INTERFACE DURING THE GROWTH OF A NEW PHASE

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The growth of a new phase in a one-component system is investigated. The relation between the shape and the velocity of a growing interface is formulated. Explicit dependences of this velocity on transport phenomena across and along the interface are derived by methods of the nonequilibrium thermodynamics of the discontinuity surface. Some special cases are discussed.

Phase changes (condensation, crystallization, solidification, *etc.*) belong to processes whose complex and satisfactory phenomenological dynamic theory has not been so far elaborated. Strictly speaking, the phenomenological methods are employed mainly for the description of the phase equilibrium only, whereas the dynamic processes are studied by methods of the statistical physics. This, after all, is not too much surprising, since there are numerous factors which affect these first-order phase transitions. So, *e.g.*, the growth of a crystal from liquid and properties of this crystal depend on surface processes at the solid–liquid interface, on the character of temperature and concentration fields in the vicinity of the interface, on the hydrodynamic convection in the fluid, *etc.*[1]

In the first approximation, any phase change process can be separated into two steps[2]: *1*) formation of the nucleus of the new phase, *2*) growth of this new phase. Whereas the first step is characterized by large deviations from the thermodynamic equilibrium and by high velocities of macroscopic processes, in the second step the deviations and velocities are usually by an order lower[3]. The first, resp. the second step belongs subsequently to turbulent, resp. slow nonequilibrium processes. Due to this fact, the growth of a new phase can be studied by methods of the linear nonequilibrium thermodynamics, which will be demonstrated in this work.

First let us formulate the problem investigated: We have a one-component system whose boundary conditions are well defined and whose total mass is constant. The system investigated is in two continuous phases. Within the range of the individual, bulk phases and also between them (across the interface), we can observe the conjugated heat and mass transfer and viscous dissipation. Due to the nonequilibrium state, the moving interface exhibits jumps not only in the first derivatives of the Gibbs free energy, but also in other variables. Now we are trying to answer the following

question: How does the time-space evolution of the growing interface depend on the processes considered? In other words, we are searching for a differential equation which would describe the shape of this interface.

It follows from the above mentioned facts that the given problem can be solved by methods of the phenomenological nonequilibrium thermodynamics of the discontinuity surface. We are going to use this theory in the form employed earlier in papers by Waldmann[4,5], Bedeaux, Albano and Mazur[6] and in papers[7-10].

MATHEMATICAL

The equation of a moving interface $\mathscr{B}$ which is imbedded in the three-dimensional Euclidean space (E_3), is either

$$f(x^1, x^2, x^3, t) = 0\,, \tag{1}$$

where x^i's form the set of Carthesian coordinates and t is time, or it possesses the parametric form

$$x^i = x^i(\xi^1, \xi^2, t)\,, \tag{2}$$

where ξ_Λ ($\Lambda = 1, 2$) are so called Gaussian parameters.

We can always choose such a set of curvilinear coordinates $y^i = y^i(x, t)$ ($i = 1, 2, 3$), so that it holds $y^1 = \xi^1$, $y^2 = \xi^2$ and y^3 corresponds with the null form of (1) (ref.[11]). In this work we shall limit ourselves to the orthogonal curvilinear coordinates y^1, y^2, $y^3 = f|\mathrm{grad}\, f|^{-1}$ ($= 0$).

The contravariant base vectors are

$$\boldsymbol{a}^i = \frac{\partial y^i}{\partial x^k}\,\mathbf{e}_k \tag{3}$$

or

$$\boldsymbol{a}^\Lambda = \frac{\partial y^\Lambda}{\partial x^k}\,\mathbf{e}_k = B^\Lambda_k \mathbf{e}_k\,, \quad \boldsymbol{a}^3 = \mathrm{grad}\, f/|\mathrm{grad}\, f| = \boldsymbol{n} = n^\perp_k \mathbf{e}_k\,, \tag{4}$$

where $\mathbf{e}_k$ are unit vectors of Carthesian coordinates, $\boldsymbol{n}$ is unit normal of the interface $\mathscr{B}$ and $\perp$ denotes its Carthesian components. We employ the usual (Einstein) summation convention over repeating indexes (latin indexes are equal to 1, 2, 3 and Greek ones to 1, 2).

The orthogonality conditions (*i.e.* $(\boldsymbol{a}^i \,.\, \boldsymbol{a}^j) = 0$ for $i \neq j$) lead to

$$B^\Lambda_k B^\Gamma_k = 0\,(\Lambda \neq \Gamma)\,, \quad B^\Lambda_k n^\perp_k = 0\,. \tag{5}$$

Similarly, for covariant base vectors it holds

$$\boldsymbol{a}_j = \frac{\partial x^k}{\partial y^j}\,\mathbf{e}_k \tag{6}$$

or

$$\boldsymbol{a}_\Lambda = \frac{\partial x^k}{\partial y^\Lambda}\,\mathbf{e}_k = B^k_\Lambda \mathbf{e}_k\,, \quad \boldsymbol{a}_3 = \boldsymbol{n} = n^\perp_k \mathbf{e}_k\,,$$

$$B^k_\Lambda B^k_\Gamma = 0 \quad (\Lambda \neq \Gamma)\,, \quad B^k_\Lambda n^\perp_k = 0\,. \tag{7}$$

Co- and contravariant fundamental (metric) tensors are

$$g_{ij} = (\boldsymbol{a}_i \,.\, \boldsymbol{a}_j)\,, \quad g^{ij} = (\boldsymbol{a}^i \,.\, \boldsymbol{a}^j) \tag{8}$$

i.e.,

$$\begin{aligned} g_{ij} &= g^{ij} = 0 \quad (i \neq j) \\ g_{11} &= B^k_1 B^k_1 = (B^1_k B^1_k)^{-1} = (g^{11})^{-1} \\ g_{22} &= B^k_2 B^k_2 = (B^2_k B^2_k)^{-1} = (g^{22})^{-1} \\ g_{33} &= (g^{33})^{-1} = 1 \end{aligned} \tag{9}$$

and $g_{\Lambda\Gamma}$ and $g^{\Lambda\Gamma}$ are metric tensors of the interface B. Further it holds (Eqs (4)–(8))

$$B^\Lambda_k B^i_\Lambda = B^i_k = (\delta_{kj} - n^\perp_k n^\perp_j)\,, \tag{10}$$

where δ_{kj} are Kronecker's symbols. The vectors and tensors are given by

$$\begin{aligned} \boldsymbol{v} &= v^\perp_k \mathbf{e}_k = v^k \boldsymbol{a}_k = v_k \boldsymbol{a}^k \\ \mathbf{T} &= T^\perp_{kj} \mathbf{e}_k \otimes \mathbf{e}_j = T^{kj} \boldsymbol{a}_k \otimes \boldsymbol{a}_j = T_{kj} \boldsymbol{a}^k \otimes \boldsymbol{a}^j\,, \end{aligned} \tag{11}$$

where $v^k(T^{kj})$ and $v_k(T_{kj})$ are contra- and covariant components and $\otimes$ denotes the dyadic product.

Relations (3)–(11) make it possible to assign surface quantities to any vector and tensor of E_3 as well as they enable an inverse assignment. It follows from Eqs (3)–(11) that any vector $\boldsymbol{v}$ of E_3 at an interface point possesses its surface (tangential) part $\boldsymbol{v}_T$ and its part normal to B at this point ($\boldsymbol{v}_N$):

$$\begin{aligned} \boldsymbol{v} &= \boldsymbol{v}_N + \boldsymbol{v}_T\,, \\ \boldsymbol{v}_N &= v^3 \boldsymbol{a}_3 = v_3 \boldsymbol{a}^3 = n^\perp_k n^\perp_j v^\perp_j \mathbf{e}_k = \boldsymbol{n}(\boldsymbol{n} \,.\, \boldsymbol{v}) = \boldsymbol{n} v_N \\ \boldsymbol{v}_T &= v^\Lambda \boldsymbol{a}_\Lambda = v_\Lambda \boldsymbol{a}^\Lambda = B^k_j v^\perp_j \mathbf{e}_k = [(\mathbf{I} - \boldsymbol{n} \,.\, \boldsymbol{n}) \,.\, \boldsymbol{v}]\,, \end{aligned} \tag{12}$$

where $\mathbf{I}$ is unit tensor.

Similarly, it holds for the operator $\nabla = \boldsymbol{a}^k \, \partial/\partial y^k = \mathbf{e}_k \, \partial/\partial x^k$:

$$\nabla = \nabla_N + \nabla_T , \tag{13}$$

$$\nabla_N = \boldsymbol{a}^3 \frac{\partial}{\partial y^3} = \mathbf{e}_k n_k^\perp n_j^\perp \frac{\partial}{\partial x^j} = \boldsymbol{n}(\boldsymbol{n} \,.\, \nabla) ,$$

$$\nabla_T = \boldsymbol{a}^\Lambda \frac{\partial}{\partial y^\Lambda} = \mathbf{e}_k(\delta_{kj} - n_k^\perp n_j^\perp) \frac{\partial}{\partial x^j} = \left[(\mathbf{I} - \boldsymbol{n} \otimes \boldsymbol{n}) \,.\, \nabla\right] .$$

In the same manner we can decompose any tensor $\mathbf{T}$:

$$\mathbf{T} = \mathbf{T}_N + \mathbf{T}_T$$

$$\begin{aligned}
\mathbf{T}_N &= T_{\Lambda 3} \boldsymbol{a}^\Lambda \otimes \boldsymbol{a}^3 + T_{3\Lambda} \boldsymbol{a}^3 \otimes \boldsymbol{a}^\Lambda + T_{33} \boldsymbol{a}^3 \otimes \boldsymbol{a}^3 = \\
&= T^{\Lambda 3} \boldsymbol{a}_\Lambda \otimes \boldsymbol{a}_3 + T^{3\Lambda} \boldsymbol{a}_3 \otimes \boldsymbol{a}_\Lambda + T^{33} \boldsymbol{a}_3 \otimes \boldsymbol{a}_3 = \\
&= \{(\delta_{kn} - n_k^\perp n_n^\perp) \, T_{nm}^\perp n_m^\perp n_j^\perp + n_k^\perp n_n^\perp T_{nm}^\perp (\delta_{mj} - n_m^\perp n_j^\perp) + \\
&+ n_k^\perp n_n^\perp T_{nm}^\perp n_m^\perp n_j^\perp\} \, \mathbf{e}_k \otimes \mathbf{e}_j = \\
&= \{T_{km}^\perp n_m^\perp n_j^\perp + n_k^\perp n_n^\perp T_{nj}^\perp - n_k^\perp n_n^\perp T_{nm}^\perp n_m^\perp n_j^\perp\} \, \mathbf{e}_k \otimes \mathbf{e}_j = \\
&= \left[\mathbf{T} \,.\, \boldsymbol{n}\right] \otimes \boldsymbol{n} + \boldsymbol{n} \otimes \left[\boldsymbol{n} \,.\, \mathbf{T}\right] - \boldsymbol{n} \otimes \boldsymbol{n} \,.\, \mathbf{T} \,.\, \boldsymbol{n} \otimes \boldsymbol{n} ,
\end{aligned}$$

$$\begin{aligned}
\mathbf{T}_T &= T_{\Lambda\Gamma} \boldsymbol{a}^\Lambda \otimes \boldsymbol{a}^\Gamma = T^{\Lambda\Gamma} \boldsymbol{a}_\Lambda \otimes \boldsymbol{a}_\Gamma = \\
&= (\delta_{kn} - n_k^\perp n_n^\perp) \, T_{nm}^\perp (\delta_{mj} - n_m^\perp n_j^\perp) \, \mathbf{e}_k \otimes \mathbf{e}_j = \\
&= (\mathbf{I} - \boldsymbol{n} \otimes \boldsymbol{n}) \,.\, \mathbf{T} \,.\, (\mathbf{I} - \boldsymbol{n} \otimes \boldsymbol{n}) .
\end{aligned}$$

RESULTS

The interface $\mathscr{B}$ defined by Eq. (*1*) and by the initial condition $f(\boldsymbol{x}, 0) = F(\boldsymbol{x}) = 0$ must satisfy the relation[6]

$$\frac{{}^s\mathrm{d}f}{\mathrm{d}t} = 0 , \tag{14}$$

where ${}^s\mathrm{d}*/\mathrm{d}t$ is the so called "surface" material derivative

$$\frac{{}^s\mathrm{d}*}{\mathrm{d}t} = \left(\frac{\partial *}{\partial t}\right)_{\boldsymbol{x}} + (\boldsymbol{v}^s \,.\, \mathrm{grad} *) . \tag{15}$$

The symbol $*$ denotes an arbitrary variable and $\boldsymbol{v}^s$ is the surface velocity, *i.e.*, the velocity of points of the interface (Eq. (*2*)).

Thus, the form of the required differential equation is (Eqs (*12*)–(*15*))

$$\frac{\partial f}{\partial t} + (\boldsymbol{v}_N^s \cdot \nabla_N f) + (\boldsymbol{v}_T^s \cdot \nabla_T f) = 0 . \qquad (16)$$

The effect of individual processes, which proceed in the system investigated, are taken into account in this relation through the dependence of the surface velocity on state and dissipative variables. Similarly as in the "volume" case, for planar objects the velocity $\boldsymbol{v}^s$ (or its parts $\boldsymbol{v}_N^s$ and $\boldsymbol{v}_T^s$) must also be searched for among solutions of the equation of motion (or the momentum balance). The general form of the momentum balance of the interface is[7,8]

$$\frac{\partial \varrho^s \boldsymbol{v}^s}{\partial t} + \operatorname{div}(\varrho^s \boldsymbol{v}^s \otimes \boldsymbol{v}^s - \mathbf{P}^s) + [\![J_N \boldsymbol{v} - \boldsymbol{p}]\!] = \varrho^s \boldsymbol{f} , \qquad (17)$$

where $[\![\ ]\!]$ denotes the jump of the enclosed quantity at the interface $\mathscr{B}$:

$$[\![Y]\!] = Y^+ - Y^- , \qquad (18)$$

where the quantity Y^+ (Y^-) is measured in the bulk phase I (II) which is in contact with the positive (negative) side of $\mathscr{B}$, ϱ^s is the surface density, $\mathbf{P}^s$ is tensor of the surface tension, $\boldsymbol{J}^+$ and $\boldsymbol{J}^-$ are interface mass fluxes:

$$\boldsymbol{J}^\pm = \varrho^\pm (\boldsymbol{v}^\pm - \boldsymbol{v}^s) . \qquad (19)$$

This relation represents two equations – one for the superscript $^+$ and the other for the superscript $^-$ (this shorthand notation will be used in the following). J_N is the magnitude of the normal component of $\boldsymbol{J}$, *i.e.*, $J_N^\pm = (\boldsymbol{n} \cdot \boldsymbol{J}^\pm) \cdot \boldsymbol{v}^\pm$ is the volume velocity, $\boldsymbol{p}^\pm = [\boldsymbol{n} \cdot \mathbf{P}^\pm]$ is the stress vector ($\mathbf{P}^\pm$ is the stress tensor), $\boldsymbol{f}$ is the intensity of external body forces. In the following we shall also use "mean values" of a quantity at $\mathscr{B}$:

$$\langle Y \rangle = \tfrac{1}{2}(Y^+ + Y^-) . \qquad (20)$$

Eq (*17*) must be solved in accordance with mass and energy balance and phenomenological equations. In a general case, the solution of this complicated system of partial differential equations is impossible. However, the nonequilibrium thermodynamics of the discontinuity surface[7,8] supplies us with another, less complicated manner of expressing $\boldsymbol{v}_N^s$ and $\boldsymbol{v}_T^s$. These quantities, or more precisely $(\langle \boldsymbol{v}_T \rangle - \boldsymbol{v}_T^s)$ and $(\langle \boldsymbol{v}_N \rangle - \boldsymbol{v}_N^s)$ terms, belong to dissipative parameters of the system investigated and as such they can be obtained directly from the phenomenological equations.

The mutual relation between these two methods can be illustrated on a rather simplified case, namely when it can be assumed that the surface density and surface

viscosity are negligibly small, *i.e.*, when it holds

$$\varrho^s = 0\,, \quad \mathbf{P}^s = (\mathbf{I} - \boldsymbol{n} \otimes \boldsymbol{n})\,\gamma\,, \tag{21}$$

where γ is the surface tension.

On using assumption (*21*), the mass balance[7,8] reduces to the form

$$[\![J_N]\!] = 0 \tag{22}$$

or

$$J_N^+ = J_N^-\,.$$

The flux J_N^+ leads to an increase in the mass of phase I, the flux J_N^- leads to a decrease in the mass of phase II. Basically, Eq. (*22*) states that the mass influx of the growing phase I is equal to the mass outflux of phase II. Thus, the quantity $\langle J_N \rangle$ $(= J_N^+ = J_N^-)$ is an unambiguous indicator of growth of the new phase.

If we insert the constitution assumptions (*21*) and relation (*22*) into Eq. (*17*) and separate it according to the rules outlined in the preceding paragraph into its normal and tangential parts, we obtain

$$-\gamma \operatorname{div} \boldsymbol{n} + [\![_R p_N]\!] + [\![_D p_N]\!] - \langle J_N \rangle\, [\![v_N]\!] = 0\,, \tag{23}$$

$$\nabla_T \gamma + [\![_D \mathbf{p}_T]\!] + [\![_R \mathbf{p}_T]\!] - \langle J_N \rangle\, [\![\mathbf{v}_T]\!] = 0\,, \tag{24}$$

where the subscript $_{R(D)}$ denotes the reversible (dissipative) part of the stress. In a static case of two fluids, Eq. (*23*) assumes the usual form of the Laplace equation[6]. Besides other things, Eq. (*24*) illustrates also the fact that the gradient of the surface tension can generate convective fluxes.

Under assumptions (*21*), it follows from the energy and entropy balances and from the hypothesis of local equilibrium[7-10] that the form of the entropy production σ^s of the interface $\mathscr{B}$ is

$$\begin{aligned}
\sigma^s = {} & \frac{1}{T^s}\left(\{[\![_D \mathbf{p}_T]\!] - \langle J_N \rangle\, [\![\mathbf{v}_T]\!]\} \cdot (\langle \mathbf{v}_T \rangle - \mathbf{v}_T^s)\right) + \\
& + \frac{1}{T^s}\left(\langle {}_D \mathbf{p}_T \rangle \cdot [\![\mathbf{v}_T]\!]\right) - \frac{1}{(T^s)^2}\left(\mathbf{J}_{QT}^s \cdot (\operatorname{grad} T^s)_T\right) + \\
& + \frac{1}{T^s}\left(\{[\![_D \mathbf{p}_N]\!] - \langle J_N \rangle\, [\![\mathbf{v}_N]\!]\} \cdot (\langle \mathbf{v}_N \rangle - \mathbf{v}_N^s)\right) + \frac{1}{T^s}\left(\langle {}_D \mathbf{p}_N \rangle \cdot [\![\mathbf{v}_N]\!]\right) + \\
& + [\![j_{QN}]\!]\left(\left\langle \frac{1}{T} \right\rangle - \frac{1}{T^s}\right) + \langle j_N \rangle \left[\!\!\left[\frac{1}{T} \right]\!\!\right],
\end{aligned}$$

where j_Q^s ($j_Q^\pm$) is the "surface" ("volume") heat flux and T^s ($T^\pm$) is the surface (volume) temperature.

From this expression for the entropy production we can derive, in the case of an isotropic $\mathscr{B}$, the following relations by common methods of the nonequilibrium thermodynamics

$$\mathbf{v}_N^s = \langle \mathbf{v}_N \rangle - \mathscr{K}_{11}\{[\![{}_D\mathbf{p}_N]\!] - \langle J_N \rangle [\![\mathbf{v}_N]\!]\} - \mathscr{K}_{12}\langle {}_D\mathbf{p}_N \rangle - \\ - \mathscr{K}_{13}[\![j_{QN}]\!] - \mathscr{K}_{14}\langle j_{QN} \rangle , \tag{25}$$

or

$$\mathbf{v}_N^s = \langle \mathbf{v}_N \rangle - \mathscr{K}_{11}^*\{[\![{}_D\mathbf{p}_N]\!] - \langle J_N \rangle [\![\mathbf{v}_N]\!]\} - \mathscr{K}_{12}^*\langle {}_D\mathbf{p}_N \rangle - \\ - \mathscr{K}_{13}^* \boldsymbol{n} \left(\left\langle \frac{1}{T} \right\rangle - \frac{1}{T^s} \right) - \mathscr{K}_{14}^* \boldsymbol{n} \left[\!\!\left[\frac{1}{T} \right]\!\!\right], \tag{26}$$

and

$$\mathbf{v}_T^s = \langle \mathbf{v}_T \rangle - K_{11}\{[\![{}_D\mathbf{p}_T]\!] - \langle J_N \rangle [\![\mathbf{v}_T]\!]\} - K_{12}\langle {}_D\mathbf{p}_T \rangle + K_{13} j_{QT}^s , \tag{27}$$

or

$$\mathbf{v}_T^s = \langle \mathbf{v}_T \rangle - K_{11}^*\{[\![{}_D\mathbf{p}_T]\!] - \langle J_N \rangle [\![\mathbf{v}_T]\!]\} - K_{12}^*\langle {}_D\mathbf{p}_T \rangle + K_{13}^*(\operatorname{grad} T^s)_T , \tag{28}$$

where the parameters $\mathscr{K}_{1q}$, $\mathscr{K}_{1q}^*$, K_{1q}, K_{1q}^* $(q = 1, 2, 3, 4)$ correspond with the phenomenological coefficients.

The normal component of the surface velocity can be of course expressed directly from Eq. (22) (see (18)–(20))

$$\mathbf{v}_N^s = \langle \mathbf{v}_N \rangle + \frac{\langle \varrho \rangle}{[\![\varrho]\!]} [\![\mathbf{v}_N]\!] . \tag{29}$$

Finally, if we insert relations (23), (24) into Eqs (25)–(28) and replace the terms $\{[\![{}_D\mathbf{p}_N]\!] - \langle J_N \rangle [\![\mathbf{v}_N]\!]\}$ and $\{[\![{}_D\mathbf{p}_T]\!] - \langle J_N \rangle [\![\mathbf{v}_T]\!]\}$, we obtain the dependence of the velocity $\mathbf{v}^s$ on the surface tension, on its gradient and on the shape of the interface:

$$\mathbf{v}_N^s = \langle \mathbf{v}_N \rangle - \mathscr{K}_{11}\{\boldsymbol{n}\gamma \operatorname{div} \boldsymbol{n} - [\![{}_R\mathbf{p}_N]\!]\} - \mathscr{K}_{12}\langle {}_D\mathbf{p}_N \rangle - \\ - \mathscr{K}_{13}[\![j_{QN}]\!] - \mathscr{K}_{14}\langle j_{QN} \rangle , \tag{30}$$

$$\mathbf{v}_N^s = \langle \mathbf{v}_N \rangle - \mathscr{K}_{11}^*\{\boldsymbol{n}\gamma \operatorname{div} \boldsymbol{n} - [\![{}_R\mathbf{p}_N]\!]\} - \mathscr{K}_{12}^*\langle {}_D\mathbf{p}_N \rangle - \\ - \mathscr{K}_{13}^* \boldsymbol{n} \left(\left\langle \frac{1}{T} \right\rangle - \frac{1}{T^s} \right) - \mathscr{K}_{14}^* \boldsymbol{n} \left[\!\!\left[\frac{1}{T} \right]\!\!\right], \tag{31}$$

$$\mathbf{v}_T^s = \langle \mathbf{v}_T \rangle + K_{11}\{\nabla_T \gamma + [\![_R \mathbf{p}_T]\!]\} - K_{12}\langle {}_D\mathbf{p}_T \rangle + K_{13} \mathbf{j}_{QT}^s , \tag{32}$$

$$\mathbf{v}_T^s = \langle \mathbf{v}_T \rangle + K_{11}^*\{\nabla_T \gamma + [\![_R \mathbf{p}_T]\!]\} - K_{12}^*\langle {}_D\mathbf{p}_T \rangle + K_{13}^*(\mathrm{grad}\, T^s)_T . \tag{33}$$

In these equations, the effect of the shape of the interface is included in div $\boldsymbol{n}$, which is given by

$$\mathrm{div}\, \boldsymbol{n} = \left(\frac{1}{R_1} + \frac{1}{R_2}\right),$$

where R_1, R_2 are radii of curvature of the interface.

DISCUSSION

If we summarize our results, it is obvious that *1*) the motion and change of the form and magnitude, which was denoted jointly as the "shape" of the interface, are expressed through Eq. (*16*); *2*) the effect exerted on the shape by processes proceeding in the system investigated is expressed in Eq. (*16*) implicitly through the velocity $\mathbf{v}^s$; *3*) The explicit dependence of $\mathbf{v}^s$ on these processes is given by relations (*25*)–(*33*).

All these explicit dependences can be written in the unified form

$$\mathbf{v}_N^s = \langle \mathbf{v}_N \rangle + \boldsymbol{F}^N(\ldots) \tag{34}$$

$$\mathbf{v}_T^s = \langle \mathbf{v}_T \rangle + \boldsymbol{F}^T(\ldots) \tag{35}$$

where $\boldsymbol{F}^N$, $\boldsymbol{F}^T$ are linear functions of certain auxiliary parameters. If we could not employ the basic axiom of the nonequilibrium thermodynamics, *i.e.*, the law of linearity, then relations (*34*), (*35*) would assume the form:

$$\mathbf{v}_N^s = \langle \mathbf{v}_N \rangle + \mathscr{F}^N(\ldots), \quad \mathbf{v}_T^s = \langle \mathbf{v}_T \rangle + \mathscr{F}^T(\ldots),$$

where F^N, F^T correspond with the so called response functionals.

If the growing phase is solid (*i.e.*, during crystallization or solidification), then the relations derived can be simplified. We can namely assume that this phase is in a mechanical equilibrium (*i.e.*, $\mathbf{v}^+ = 0$), so that, *e.g.*, it follows from Eq. (*29*)

$$\mathbf{v}_N^- = \left(1 - \frac{\varrho^+}{\varrho^-}\right)\mathbf{v}_N^s ,$$

which is a boundary condition employed commonly in crystallization studies.

All "volume" quantities in Eqs (*34*), (*35*) can be in principle derived from equations valid for volume phases. As a result, common dimensionless criteria (*e.g.*, Granshof's, Rayleigh's, Bond's) employed in studies of phase transitions are included implicitly in relations (*34*), (*35*). Similarly, the effect of external volume forces is included in Eqs (*34*), (*35*), too.

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