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## Effect of density change at crystallization on a one-dimensional heat balance equation at solid-liquid interface

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In this paper, we study how we should treat a steady-state interface between homogeneous crystal and melt phases, where steady temperature gradients are present at both sides. In particular, keeping the geometry of Czochralski method in mind, we study a correction for the heat balance equation at the interface between the two phases. We show that a negative term proportional to the third power of the pulling velocity, which is caused by the density difference between the two phases, is added to the heat balance equation.

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### 1. Introduction

For a long time, it has been considered that the type of defects in the Si crystal grown by the Czochralski (CZ) method with the pulling rate  $V$  is determined by the temperature gradient in crystal  $G_S$  or  $V/G_S$ . In Ref. 1, Voronkov suggested that the type of point defects in the Si crystal is governed by  $V/G_S$ . As already known for the floating zone method of Si crystal growth, the defects become interstitial if  $V/G_S$  is larger than a certain value. In contrast, they become vacancies if  $V/G_S$  is smaller than that value. Thus, defect free crystals can be grown in a limited range of  $V/G_S$ . Voronkov and Falster later refined<sup>2</sup> the Voronkov's work.<sup>1</sup> They made a detailed analysis giving a support to Voronkov's criterion.<sup>3</sup> Other groups have also analyzed the dependence of defects type on  $V/G_S$ .<sup>4-6</sup>

$V$  and  $G_S$  are intrinsically interrelated with each other. Taking account of their interrelation, Vanhellefont have recently reconsidered the Voronkov's criterion critically.<sup>7</sup> Abe and Takahashi have shown that the type of point defects is governed only by  $G_S$ , which is inconsistent with the previous studies.<sup>1-6</sup> The discrepancy between the two results is probably caused because the different geometries of apparatuses were

analyzed together.

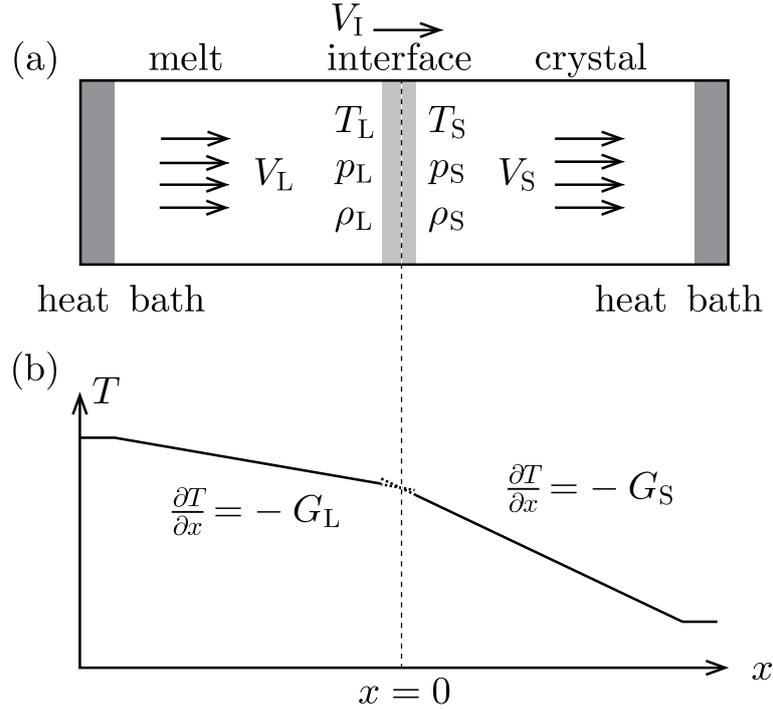
In the CZ method, the relationship between the temperature gradients and the growth rate is given by the energy conservation law:  $k_S G_S - k_L G_L = L\rho V$ , where  $G_L$  is the temperature gradient in melt,  $L$  is the latent heat,  $\rho$  is the density, and  $k_S$  and  $k_L$  represent the thermal conductivities of crystal and melt, respectively. In this simplified conservation law, the density difference between the crystal and melt is neglected, and  $G_S$  is sometimes treated as a control parameter. However,  $V$  becomes large with increasing  $G_S$ , so that  $G_S$  is not a parameter we can control directly. The temperature gradients in the crystal and melt have been measured directly.<sup>9–14</sup> Although the correlation between  $G_S$  and  $V$  is positive in Refs. 4–6, 16, 17, the negative correlation between  $G_S$  and  $V$  is reported,<sup>12, 18</sup> which is against with the simplified conservation of energy at the interface. It is suggested that the negative correlation may be caused by the mass transfer,<sup>18</sup> but we think that the neglect of the difference of density between the melt and crystal is one of the main reasons for the disagreement.

Previously, Mori et al<sup>19</sup> developed a non-equilibrium molecular dynamics simulation method of crystal/melt interface in the geometry of the CZ method using the Lennard-Jones system. In the model, the pulling rate of the crystal is set to  $V_S$  and the total amount of materials is conserved. Since the density difference between the crystal and melt is taken into account,  $V_L$  is given by  $V_L = \rho_s V_S / \rho_L$ . The temperatures at the crystal and melt side boundaries are kept constant by heat baths at the ends of the system. The temperature gradients,  $G_L$  and  $G_S$ , are determined as functions of the interface position when the system reach to the steady growth. In this simulation, the temperature gradient  $G_S$  was an increasing function of the interface position, but the sign of correlation between  $G_S$  and  $V_S$  was not determined.

In this paper, we extend a previous hydrothermodynamic formulation<sup>24</sup> to the crystal/melt interface in the geometry of the CZ method. We add the correction caused by the density difference between the crystal and melt to the simplified energy conservation law starting from microscopic conservation equations. In Sec. 2, we introduce model. In Sec. 3 we show our results. In Sec. 5, we summarize our results.

## 2. Model

We consider a crystal/melt coexistence state and a flat interface moving steadily as shown in Fig. 1(a). Mass flows in the melt and crystal at the interface are given by  $V_L$  and  $V_S$ , respectively.  $V_I$  is the the steady interface velocity. The pressures in the melt



**Fig. 1.** Schematic picture of (a) system under consideration and (b) temperature distribution.  $V_I$ ,  $V_S$ , and  $V_L$  are steady velocities of interface, the pulling rate, and the mass flow in melt, respectively. The pressures at the liquid and solid sides are given by  $p_L$  and  $p_S$ , respectively. The densities  $\rho_S$  and  $\rho_L$  are also defined at both sides of the interface. For latter convenience, the temperatures  $T_L$  and  $T_S$  at both side of the interface are introduced. we set  $x = 0$  at the center of interface.

and crystal at the interface are given by  $p_L$  and  $p_S$ , respectively. Figure 1(b) shows the temperature distribution in our model schematically. Corresponding to the CZ method, temperature decreases monotonically from the melt to the crystal.

As already shown in Ref.,<sup>24</sup> the system is modeled as a Navier-Stokes-Fourier liquid including the interface. The general equations are given by

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_i}{\partial x_i} = 0, \tag{1}$$

$$\frac{\partial \rho u_i}{\partial t} + \frac{\partial \rho u_i u_j}{\partial x_j} = \frac{\partial \sigma_{ij}}{\partial x_j} + X_i, \tag{2}$$

$$\frac{\partial}{\partial t} \left( \rho e + \frac{\rho}{2} u^2 \right) + \frac{\partial}{\partial x_i} \left[ \left( \rho e + \frac{\rho}{2} u^2 \right) u_i \right] = \frac{\partial \sigma_{ij} u_j}{\partial x_i} + X_i u_i - \frac{\partial q_i}{\partial x_i}, \tag{3}$$

where  $u_i$ ,  $x_i$ ,  $\sigma_{ij}$ ,  $X_i$ ,  $e$ , and  $q_i$  represent the flow velocity vector, the position vector, the stress tensor, the external force vector, the specific internal energy, and the heat flux vector, respectively. In Eq. (3),  $u_k u_k$  is abbreviated as  $u^2$ . The stress tensor  $\sigma_{ij}$  and

the heat flux vector  $q_i$  are given by

$$\sigma_{ij} = -p\delta_{ij} + \eta_s \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\delta_{ij} \frac{\partial u_k}{\partial x_k} \right) + \zeta \delta_{ij} \frac{\partial u_k}{\partial x_k}, \quad (4)$$

$$q_i = -k \frac{\partial T}{\partial x_j}, \quad (5)$$

where  $p$  is the hydrostatic pressure,  $\eta_s$  is the shear viscosity,  $\zeta$  is the bulk viscosity, and  $k$  is the heat conductivity. In the case of one-dimensional system, Eqs (1)-(5) are reduced to

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} = 0, \quad (6)$$

$$\frac{\partial \rho u}{\partial t} + \frac{\partial (\rho u^2)}{\partial x} = -\frac{\partial p}{\partial x} + \frac{\partial}{\partial x} \left( \eta_L \frac{\partial u}{\partial x} \right), \quad (7)$$

$$\frac{\partial}{\partial t} \left( \rho e + \frac{\rho}{2} u^2 \right) + \frac{\partial}{\partial x} \left[ \left( \rho e + \frac{\rho}{2} u^2 \right) u \right] = -\frac{\partial (p u)}{\partial x} + \frac{\partial}{\partial x} \left( \eta_L \frac{\partial u}{\partial x} u \right) + \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right), \quad (8)$$

where  $x$  is the coordinate perpendicular to the interface, the origin of the  $x$  coordinate is set at the center of the interface, and  $\eta_L \equiv \eta_s/3 + \zeta$  is the longitudinal viscosity. In the case of the steady growth, when we rewrite Eqs. (6)-(8) in terms of  $z \equiv x - V_I t$ , these equations are given by

$$-V_I \frac{d\rho}{dz} + \frac{d\rho u}{dz} = 0, \quad (9)$$

$$-V_I \frac{d\rho u}{dz} + \frac{d(\rho u^2)}{dz} = -\frac{dp}{dz} + \frac{d}{dz} \left( \eta_L \frac{du}{dz} \right), \quad (10)$$

$$-V_I \frac{d}{dz} \left( \rho e + \frac{\rho}{2} u^2 \right) + \frac{d}{dz} \left[ \left( \rho e + \frac{\rho}{2} u^2 \right) u \right] = -\frac{d(pu)}{dz} + \frac{d}{dz} \left( \eta_L \frac{du}{dz} u \right) + \frac{d}{dz} \left( k \frac{dT}{dz} \right). \quad (11)$$

### 3. Results and discussion

When we integrate Eqs. (9)-(10) from the melt side to the crystal side at the interface, we get the following equations:

$$\rho_S V_S - \rho_L V_L = (\rho_S - \rho_L) V_I, \quad (12)$$

$$\rho_S V_S^2 - \rho_L V_L^2 - (\rho_S V_S - \rho_L V_L) V_I = -p_S + p_L. \quad (13)$$

Equation (11) is reduced as

$$\begin{aligned} & -V_I \left[ \left( \rho_S e_S + \frac{\rho_S}{2} V_S^2 \right) - \left( \rho_L e_L + \frac{\rho_L}{2} V_L^2 \right) \right] + \left( \rho_S e_S + \frac{\rho_S}{2} V_S^2 \right) V_S - \left( \rho_L e_L + \frac{\rho_L}{2} V_L^2 \right) V_L \\ & = -p_S V_S + p_L V_L - k_S G_S + k_L G_L. \end{aligned} \quad (14)$$

Comparing Eq. (14) with Ref. 24, a term  $-k_S G_S + k_L G_L$  is added in the right hand side of Eq. (14). From Eqs. (12) and (13), the difference between  $p_S$  and  $p_L$  is given by

$$p_S - p_L = \frac{(V_L - V_S)^2}{v_L - v_S}, \quad (15)$$

where  $v_L$  and  $v_S$  are the specific volumes defined as  $v_L = 1/\rho_L$  and  $v_S = 1/\rho_S$ . Eq. (15) means that irrespective of the direction of the mass flow, the denser phase has higher pressure than the other.

### 3.1 Correction for heat balance equation

When we eliminate  $V_I$  from Eq. (14), the difference in the specific enthalpies is given by

$$h_S - h_L = \frac{1}{2}(v_L + v_S)(p_S - p_L) - \frac{v_L - v_S}{V_L - V_S}(k_S G_S - k_L G_L), \quad (16)$$

where the specific enthalpies,  $h_S$  and  $h_L$ , are defined as  $h_S = e_S + p_S v_S$  and  $h_L = e_L + p_L v_L$  (see the detail derivation of Eq. (16) in Appendix A). The term proportional to  $-k_S G_S + k_L G_L$  is added in Eq. (16), which is different from a previous study.<sup>24</sup> When we assume that  $(\rho_S - \rho_L)V_I$  is enough small to be neglected.<sup>24</sup> Eqs. (12) and (15) are reduced to

$$V_L = \frac{\rho_S V_S}{\rho_L} = \frac{v_L V_S}{v_S}, \quad (17)$$

$$p_S - p_L = (v_L - v_S) \left( \frac{V_S}{v_S} \right)^2. \quad (18)$$

Using Eqs. (17) and (18), Eq. (16) is expressed as

$$k_S G_S - k_L G_L = \frac{V_S}{v_S} \left[ (h_L - h_S) + \frac{1}{2}(v_L^2 - v_S^2) \left( \frac{V_S}{v_S} \right)^2 \right] \quad (19)$$

$$= \rho_S V_S \left\{ (h_L - h_S) + \frac{1}{2} \left[ \left( \frac{\rho_S}{\rho_L} \right)^2 - 1 \right] V_S^2 \right\}. \quad (20)$$

If the difference between the specific enthalpies ( $h_L - h_S$ ) is identified with the latent heat  $L$ , Eq. (20) may be the heat balance equation with a correction caused by the density difference. However, we need to consider the difference in the specific enthalpies carefully. We expand  $h_S$  and  $h_L$  around a point  $(T_0, p_0)$  on the coexistence curve. The difference in the specific enthalpy ( $h_L - h_S$ ) is expressed as

$$h_L - h_S = L + c_L(T_L - T_0) - c_S(T_S - T_0) + v_L(p_L - p_0) - v_S(p_S - p_0) \quad (21)$$

where  $L$  is the latent heat defined as  $L = h_L(T_0, p_0) - h_S(T_0, p_0)$ , and  $c_L$  and  $c_S$  are the specific heats of the melt and crystal, respectively. When we use Eq. (16), we get the

following expression:

$$k_S G_S - k_L G_L = \rho_S V_S [L + c_L(T_L - T_0) - c_S(T_S - T_0)] + V_S \left( \frac{\rho_S}{\rho_L} - 1 \right) \left( \frac{p_L + p_S}{2} - p_0 \right). \quad (22)$$

When  $p_0 = (p_S + p_L)/2$ , the last term in Eq. (22) is eliminated. Here, we consider Clausius-Clapeyron equation,  $dp/dT = L/T_0(v_L - v_S)$ . When  $p_S$  is very close to  $p_L$ , the coexistence line is linear between  $p_S$  and  $p_L$ . The Clausius-Clapeyron equation is approximated as

$$\frac{p_L - p_0}{T^e(p_L) - T_0} = \frac{p_S - p_0}{T^e(p_S) - T_0} = \frac{L}{T_0(v_L - v_S)}, \quad (23)$$

where  $T^e(p_L)$  and  $T^e(p_S)$  represent the melting temperatures at  $p_L$  and  $p_S$ , respectively. From Eqs. (17), (18), and (23),  $k_S G_S - k_L G_L$  is given by

$$k_S G_S - k_L G_L = \rho_S V_S \{L^* + c_L[T_L - T^e(p_L)] - c_S[T_S - T^e(p_S)]\} - \frac{1}{2} \frac{(c_L + c_S)T_0}{L^*} \left( \frac{\rho_S}{\rho_L} - 1 \right)^2 \rho_S V_S^3, \quad (24)$$

where  $L^*$  is given by

$$L^* = h_L \left( T_0, \frac{p_L + p_S}{2} \right) - h_S \left( T_0, \frac{p_L + p_S}{2} \right) \quad (25)$$

Stability conditions of the crystal and melt phases, which are satisfied for the CZ method, are given by  $T_S - T^e(p_S) \leq 0$  and  $0 \leq T_L - T^e(p_L)$ . Thus, we find that both the second and third terms in the first bracket in the right hand side of Eq. (24) are positive and the contribution of the last term proportional to  $V_S^3$  is negative. In Eq. (20), the sign of the term proportional to  $V_S^3$  seems to reverse with the change in the magnitude relation between  $\rho_S$  and  $\rho_L$ . However, when we take account of the difference in the enthalpies more precisely, the dependence of  $k_S G_S - k_L G_L$  is negative irrespective of the magnitude relation between  $\rho_S$  and  $\rho_L$  as shown in Eq. (24).

### 3.2 Entropy production

We also consider the entropy production. According to a standard method of nonequilibrium thermodynamics,<sup>25</sup> we start with the Gibbs relation  $Td(\rho s) = d(\rho e) - \mu d\rho$ , where  $s$  is the specific entropy and  $\mu$  is the chemical potential. Using  $e = Ts - pv + u$  and Eqs. (6)-(8), we obtain

$$T \left[ \frac{\partial \rho s}{\partial t} + \frac{\partial(\rho s u)}{\partial x} \right] = \left( \eta_L \frac{\partial u}{\partial x} \right) \frac{\partial u}{\partial x} + \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right), \quad (26)$$

where we used  $d/dt = \partial/\partial t + u(\partial/\partial x)$  (see the detail derivation of Eq. (26) in Appendix B). We first rewrite Eq. (26) by  $z = x - V_I t$ . Then, after we divide the equation by  $T$  and eliminate  $V_I$  using Eq. (12), we integrate the equation between the melt and crystal at the interface. We obtain

$$(s_S - s_L) \frac{V_S - V_L}{v_S - v_L} = \int_{I_-}^{I_+} \eta_L \left( \frac{\partial u}{\partial z} \right)^2 dz + \int_{I_-}^{I_+} \frac{k}{T^2} \left( \frac{dT}{dz} \right)^2 dz, \quad (27)$$

where  $I_-$  and  $I_+$  indicate the melt and crystal sides at the interface, respectively. Although the integration region in Eq. (27) is entirely different from that in Ref.,<sup>24</sup> the meanings of both equations are same. In Eq. (27), the first term of the right hand side is entropy production caused by viscosity in the interface region, and the second term is that induced by thermal conduction. Since both of two terms are positive, the left hand side of the equation should be positive in the steady state. Using Eq (17), we find that

$$(s_S - s_L) \frac{V_S - V_L}{v_S - v_L} = (s_S - s_L) \frac{V_S}{v_S} > 0, \quad (28)$$

irrespective of the sign of  $v_S - v_L$ . Thus, at given  $V_S$ , the temperatures and pressures at the both sides of the interface are determined consistently with the second law of thermodynamics. We expand  $s$  as

$$s = s^0 + \frac{c}{T_0} \Delta T - \frac{1}{2} \frac{c}{T_0^2} \Delta T^2, \quad (29)$$

where  $s^0 = s(T_0, p_0)$ . Eq. (27) is expressed as

$$\begin{aligned} -\frac{c_S}{2} \left( \frac{\Delta T_S}{T_0^2} \right)^2 + \frac{c_L}{2} \left( \frac{\Delta T_L}{T_0^2} \right)^2 &= \frac{v_S - v_L}{V_S - V_L} \left[ \int_{I_-}^{I_+} \eta_L \left( \frac{\partial u}{\partial z} \right)^2 dz + \int_{I_-}^{I_+} \frac{k}{T^2} \left( \frac{dT}{dz} \right)^2 dz \right] \\ &= \frac{v_S}{V_S} \left[ \int_{I_-}^{I_+} \eta_L \left( \frac{\partial u}{\partial z} \right)^2 dz + \int_{I_-}^{I_+} \frac{k}{T^2} \left( \frac{dT}{dz} \right)^2 dz \right]. \end{aligned} \quad (30)$$

Since  $V_S$  is in the right hand side in Eq. (30), the left hand side is positive for a pulling-up process and negative for a pulling-down process. Namely,  $c_S(T_S - T_0)^2 < c_L(T_L - T_0)^2$  for a crystallization process and  $c_S(T_S - T_0)^2 > c_L(T_L - T_0)^2$  for a melting process.

#### 4. Discussion

We estimate the correction term for the CZ-Si using Eq. (24). In the case of Si,<sup>27</sup>  $\rho_S = 2.305 \text{ kg/m}^3$  and  $\rho_L = 2.520 \text{ kg/m}^3$ . The second and third terms in the first brackets in the right hand side of Eq. (24) are neglected under assumption of a non-singular interface. When we use  $L^* = 1.787 \text{ J/kg}^{-1}$ ,  $c_L = 946 \text{ JKg}^{-1}\text{K}^{-1}$ ,  $c_S = 1000 \text{ JKg}^{-1}\text{K}^{-1}$ , and  $T_0 = 1685 \text{ K}$ ,<sup>27</sup>  $(c_L + c_S)T_0(\rho_S/\rho_L - 1)^2/2L^*$  is estimated to  $6.7 \times 10^3$ . Thus, if  $V_S$  is

in the order of a few mm/s, the the effect of the correction is less than a few percent. Unfortunately, the effect of the correction term is small in our estimation for CZ-Si, but there may be other materials which the correction term is important for.

In the above estimation, there are problems we should consider carefully. The geometry we dealt in this paper is suitable for unidirectional solidification in a thin rectangular parallelepiped cell such as a Hele-Shaw cell, but we should have considered the radius ratio of the radius of crucible  $R$  and that of growing crystal  $r$  in the case of CZ-Si growing in crucible. In addition, we neglected the effect of thermal radiation. In this paper, we did not take account of these effects to estimate the effect of the correction term on CZ-Si for simplicity. However, when we try to apply our result to experiments more precisely, we need to consider those problems more carefully. Thus, we think that the derivation of the correction term by using the condition for crucible condition and considering the effect of thermal radiation are future problems

## 5. Summary

We have successfully extended a hydrothermodynamic formulation to the crystal/melt interface in a geometry of Czochralski method. As a result, we calculated a  $V_s^3$  dependent correction term to the latent heat in a heat balance equation. In other words, we have incorporated the effect of density difference between the crystal and melt into the heat balance equation. The correction term gives a negative contribution to the latent heat. We also study the entropy production. In Eq. (30), the integration range is different from our previous study, we obtained the same magnitude relation between  $c_S(T_S - T_0)^2$  and  $c_L(T_L - T_0)^2$ .

There were a lot of studies whose constituent equations including microscopic continuum conservation equations such as Refs. 28–33. However, they did not concern the heat balance equation. Furthermore, they relied on numerical calculations to treat the complicated geometry. For example, a free surface on the melt was sometimes taken into account, and the heat radiation was incorporated in them. Namely, the heat balance equation cannot hold in its native form. Such complications lost thermodynamic transparency. In particular, the entropic considerations were not given, but I think that our approach to give additional terms one by one to a simple model helps insights and develops concept.

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### Appendix A: Derivation of Eq. (16)

By using Eq. (12), Eq. (14) is expressed as

$$\begin{aligned} & -\frac{\rho_S V_S - \rho_L V_L}{(\rho_S - \rho_L)} \left[ \left( \rho_S e_S + \frac{\rho_S}{2} V_S^2 \right) - \left( \rho_L e_L + \frac{\rho_L}{2} V_L^2 \right) \right] \\ & + \left( \rho_S e_S + \frac{\rho_S}{2} V_S^2 \right) V_S - \left( \rho_L e_L + \frac{\rho_L}{2} V_L^2 \right) V_L \\ & = -p_S V_S + p_L V_L - k_S G_S + k_L G_L. \end{aligned} \quad (\text{A}\cdot 1)$$

The terms proportional to  $e_S$  and  $e_L$  in Eq. (A.1) are reduced as

$$\begin{aligned} & \left[ -\frac{\rho_S V_S - \rho_L V_L}{(\rho_S - \rho_L)} + V_S \right] \rho_S e_S - \left[ -\frac{\rho_S V_S - \rho_L V_L}{(\rho_S - \rho_L)} + V_L \right] \rho_L e_L \\ & = \frac{\rho_S \rho_L (V_S - V_L)}{\rho_S - \rho_L} (e_S - e_L) = \frac{(V_S - V_L)}{v_S - v_L} (e_S - e_L). \end{aligned} \quad (\text{A}\cdot 2)$$

When we similarly reduce the terms proportional to  $\rho_S V_S/2$ , Thus, Eq (A.1) is given by

$$\frac{(V_S - V_L)}{v_S - v_L} \left[ (e_S - e_L) + \frac{1}{2}(V_S^2 - V_L^2) \right] = -p_S V_S + p_L V_L - k_S G_S + k_L G_L. \quad (\text{A}\cdot 3)$$

By using Eq. (A.3),  $\Delta h = h_S - h_L$  is given by

$$\begin{aligned} \Delta h & = e_S - e_L + p_S v_S - p_L v_L \\ & = \frac{(v_S - v_L)}{V_S - V_L} [(p_L V_L - p_S V_S) - (k_S G_S - k_L G_L)] - \frac{(V_S^2 - V_L^2)}{2} + p_S v_S - p_L v_L \\ & = \frac{v_S V_L - v_L V_S}{V_L - V_S} (p_S - p_L) - \frac{(V_S^2 - V_L^2)}{2} - \frac{(v_S - v_L)}{V_S - V_L} (k_S G_S - k_L G_L). \end{aligned} \quad (\text{A}\cdot 4)$$

The first and second terms in the fourth line in Eq. (A.4) are reduced as

$$\begin{aligned} & \frac{(v_S V_L - v_L V_S)}{V_L - V_S} (p_S - p_L) - \frac{(V_S^2 - V_L^2)}{2} \\ & = \frac{(V_L - V_S)^2}{2(v_L - v_S)} (v_L + v_S) = \frac{(p_S - p_L)}{2} (v_L + v_S), \end{aligned} \quad (\text{A}\cdot 5)$$

where we used Eq. (15). Thus,  $\Delta h$  is given by

$$\Delta h = \frac{1}{2} (v_L + v_S) (p_S - p_L) - \frac{(v_S - v_L)}{V_S - V_L} (k_S G_S - k_L G_L). \quad (\text{A}\cdot 6)$$

### Appendix B: Derivation of Eq. (26)

Gibbs free energy  $G(= \mu N)$  is related to energy  $E$ , pressure  $p$ , volume  $V$ , temperature  $T$ , and entropy  $S$  as  $\mu N = E + pV - TS$ . The equation is expressed as  $\rho\mu = \rho e + p - T\rho s$ , where we define  $s$  and  $v$  as  $s = S/N$  and  $v = V/N = 1/\rho$ . Thus, we obtain the following relation,

$$\rho d\mu + \mu d\rho = d(\rho e) + dp - \rho s dT - T d(\rho s). \quad (\text{B}\cdot 1)$$

On the other hand,  $dG$  is given by  $dG = -SdT + Vdp + \mu dN$ . Since  $dG = \mu dN + Nd\mu$ , we obtain the Gibbs-Duhem equation,  $Nd\mu = -SdT + Vdp$ . When we use  $\rho$ , the Gibbs-Duhem equation is expressed as

$$\rho d\mu = -(\rho s)dT + dp \quad (\text{B}\cdot 2)$$

From eqs. (B.1) and (B.2),  $\mu d\rho$  is given by  $\mu d\rho = d(\rho e) - Td(\rho s)$ . Thus, we obtain the Gibbs relation,

$$Td(\rho s) = d(\rho e) - \mu d\rho. \quad (\text{B}\cdot 3)$$

Since  $d/dt$  is related to  $\partial/\partial t$  and  $\partial/\partial x$  as  $d/dt = \partial/\partial t + u(\partial/\partial x)$ , from Eq. (B.3) we obtain

$$T \left[ \frac{\partial \rho s}{\partial t} + u \frac{\partial(\rho s)}{\partial x} \right] = \frac{d\rho e}{dt} - \mu \frac{d\rho}{dt}. \quad (\text{B}\cdot 4)$$

In the left hand side of Eq. (B.4), the second term in parenthesis is expressed as

$$u \frac{\partial(\rho s)}{\partial x} = \frac{\partial(\rho s u)}{\partial x} - \rho s \frac{\partial u}{\partial x}. \quad (\text{B}\cdot 5)$$

Equation (B.4) is modified as

$$\begin{aligned} T \left[ \frac{\partial \rho s}{\partial t} + \frac{\partial(\rho s u)}{\partial x} \right] &= \frac{d\rho e}{dt} - \mu \frac{d\rho}{dt} + T \rho s \frac{\partial u}{\partial x} \\ &= \left[ \frac{\partial(\rho e)}{\partial t} + u \frac{\partial(\rho e)}{\partial x} \right] - \mu \left[ \frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} \right] + T \rho s \frac{\partial u}{\partial x}. \end{aligned} \quad (\text{B}\cdot 6)$$

Since  $\rho e = \rho T s - p + \rho \mu$ , we obtain the following relation,

$$T \rho s \frac{\partial u}{\partial x} = \rho e \frac{\partial u}{\partial x} + p \frac{\partial u}{\partial x} - \rho \mu \frac{\partial u}{\partial x}. \quad (\text{B}\cdot 7)$$

Equation (B.6) is given by

$$\begin{aligned} T \left[ \frac{\partial \rho s}{\partial t} + \frac{\partial(\rho s u)}{\partial x} \right] &= \frac{\partial(\rho e)}{\partial t} + u \frac{\partial(\rho e)}{\partial x} - \mu \left( \frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} \right) + T \rho s \frac{\partial u}{\partial x} \\ &= \frac{\partial(\rho e)}{\partial t} + u \frac{\partial(\rho e)}{\partial x} - \mu \left( \frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} \right) + \rho e \frac{\partial u}{\partial x} + p \frac{\partial u}{\partial x} - \rho \mu \frac{\partial u}{\partial x}. \end{aligned} \quad (\text{B}\cdot 8)$$

By using  $u\partial(\rho e)/\partial x + \rho e\partial u/\partial x = \partial(\rho e u)/\partial x$ , Eq. (B.8) is expressed as

$$T \left[ \frac{\partial \rho s}{\partial t} + \frac{\partial(\rho s u)}{\partial x} \right] = \frac{\partial(\rho e)}{\partial t} + \frac{\partial(\rho e u)}{\partial x} - \mu \left[ \frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} \right] + p \frac{\partial u}{\partial x} - \rho \mu \frac{\partial u}{\partial x}. \quad (\text{B}\cdot 9)$$

From Eq. (6),  $\partial \rho/\partial t$  is given by

$$\frac{\partial \rho}{\partial t} = -\frac{\partial \rho u}{\partial x} = -u \frac{\partial \rho}{\partial x} - \rho \frac{\partial u}{\partial x}. \quad (\text{B}\cdot 10)$$

From Eqs. (8) and (B·10), Eq. (B·9) is expressed as

$$\begin{aligned} T \left[ \frac{\partial \rho s}{\partial t} + \frac{\partial(\rho s u)}{\partial x} \right] &= \frac{\partial(\rho e)}{\partial t} + \frac{\partial(\rho e u)}{\partial x} + p \frac{\partial u}{\partial x} \\ &= - \frac{\partial}{\partial t} \left( \frac{\rho u^2}{2} \right) - \frac{\partial}{\partial x} \left( \frac{\rho u^3}{2} \right) - u \frac{\partial p}{\partial x} \\ &\quad + \frac{\partial}{\partial x} \left( \eta_L \frac{\partial u}{\partial x} \right) u + \left( \eta_L \frac{\partial u}{\partial x} \right) \frac{\partial u}{\partial x} + \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right). \end{aligned} \quad (\text{B}\cdot\text{11})$$

When we use Eq. (7), we obtain the following relation,

$$\frac{\partial}{\partial x} \left( \eta_L \frac{\partial u}{\partial x} \right) = \frac{\partial \rho u}{\partial t} + \frac{\partial(\rho u^2)}{\partial x} + \frac{\partial p}{\partial x}. \quad (\text{B}\cdot\text{12})$$

Equation (B·11) is expressed as

$$\begin{aligned} T \left[ \frac{\partial \rho s}{\partial t} + \frac{\partial(\rho s u)}{\partial x} \right] &= - \frac{\partial}{\partial t} \left( \frac{\rho u^2}{2} \right) - \frac{\partial}{\partial x} \left( \frac{\rho u^3}{2} \right) + u \frac{\partial \rho u}{\partial t} + u \frac{\partial(\rho u^2)}{\partial x} \\ &\quad + \left( \eta_L \frac{\partial u}{\partial x} \right) \frac{\partial u}{\partial x} + \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right). \end{aligned} \quad (\text{B}\cdot\text{13})$$

In Eq. (B·13), the first and third terms in the right hand side are transformed as follows:

$$- \frac{\partial}{\partial t} \left( \frac{\rho u^2}{2} \right) = - \rho \frac{\partial}{\partial t} \left( \frac{u^2}{2} \right) - \frac{u^2}{2} \frac{\partial \rho}{\partial t} = - \rho u \frac{\partial u}{\partial t} - \frac{u^2}{2} \frac{\partial \rho}{\partial t}, \quad (\text{B}\cdot\text{14})$$

$$u \frac{\partial \rho u}{\partial t} = \rho u \frac{\partial u}{\partial t} + u^2 \frac{\partial \rho}{\partial t}. \quad (\text{B}\cdot\text{15})$$

Thus, Eq. (B·13) is expressed as

$$\begin{aligned} T \left[ \frac{\partial \rho s}{\partial t} + \frac{\partial(\rho s u)}{\partial x} \right] &= \frac{u^2}{2} \frac{\partial \rho}{\partial t} - \frac{\partial}{\partial x} \left( \frac{\rho u^3}{2} \right) + u \frac{\partial(\rho u^2)}{\partial x} \\ &\quad + \left( \eta_L \frac{\partial u}{\partial x} \right) \frac{\partial u}{\partial x} + \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right), \end{aligned} \quad (\text{B}\cdot\text{16})$$

By using Eq. (6), the terms in the right hand side in the first line in Eq. (B·16) are eliminated as follows:

$$\frac{u^2}{2} \frac{\partial \rho}{\partial t} - \frac{\partial}{\partial x} \left( \frac{\rho u^3}{2} \right) + u \frac{\partial(\rho u^2)}{\partial x} = - \frac{u^2}{2} \frac{\partial \rho u}{\partial x} - \frac{\partial}{\partial x} \left( \frac{\rho u^3}{2} \right) + u \frac{\partial(\rho u^2)}{\partial x} = 0 \quad (\text{B}\cdot\text{17})$$

Thus, we obtain Eq. (26).

**References**

- 1) V. V. Voronkov, *J. Cryst. Growth* **59**, 652 (1982).
- 2) V. V. Voronkov and R. Falster, *J. Cryst. Growth* **194**, 76 (1998).
- 3) V. V. Voronkov and R. Falster, *J. Appl. Phys.* **86**, 5975 (1999).
- 4) W. von Ammon, E. Dolnberger, H. Oelkrug, and H. Weidner, *J. Cryst. Growth* **151**, 273 (1995).
- 5) M. Hourai, E. Kajita, T. Nagashima, H. Fujiwara, S. Umeno, S. Sadamitsu, S. Miki, and T. Shigematsu, *Mater. Sci. Forum* **196-201**, 1713 (1995).
- 6) K. Nakamura, T. Saishoji, T. Kubota, T. Iida, Y. Shimanuki, T. Ko-tooka, and J. Tomioka, *J. Cryst. Growth* **180**, 61 (1997).
- 7) J. Vanhellemont, *J. Appl. Phys.* **110**, 063519 (2011).
- 8) T. Abe, *J. Cryst. Growth* **334**, 16 (2011).
- 9) E. Kuroda, *J. Cryst. Growth* **61**, 173 (1983).
- 10) E. Kuroda and H. Kozuka, *J. Cryst. Growth* **63**, 276 (1983).
- 11) E. Kuroda, H. Kozuka, and Y. Takano, *J. Cryst. Growth* **68**, 612 (1984).
- 12) T. Abe, *Mater. Sci. Eng. B* **73**, 16 (2000).
- 13) X. Huang, T. Taishi, T. Wang, and K. Hoshikawa, *J. Cryst. Growth* **229**, 6 (2001).
- 14) K. Kitamura, J. Furukawa, Y. Nakada, N. Ono, Y. Shimanuki, A. M. Eidenzon, N. I. Puzanov, and D. N. Puzanov, *J. Cryst. Growth* **242**, 293 (2002).
- 15) T. Abe, H. Harada, and J. Chikawa, *Physica B* **116**, 139 (1983).
- 16) A. Natsume, N. Inoue, K. Tanahashi, and A. Mori, *J. Cryst. Growth* **225**, 221 (2000).
- 17) A. Natsume, N. Inoue, and K. Tanahashi, *Microelec. Eng.* **56**, 129 (2001).
- 18) K. Shirai and T. Abe, *J. Cryst. Growth* **351** (2012) 141-148.
- 19) A. Mori, F. Shirazawa, and N. Inoue, *Russ. J. Phys. Chem.* **78**, suppl. 1 S176 (2004).
- 20) K. Kitamura, J. K. Yamamoto, N. Iyi, S. Kimura, and T. Hayashi, *J. Cryst. Growth* **116**, 327 (1992).
- 21) M. Ishimaru, S. Munetoh, T. Motooka, K. Moriguchi, and A. Shintani, *Phys. Rev. B* **58** 12583 (1998).
- 22) T. Motooka, K. Nishihira, R. Oshima, H. Nishizawa, and Hori, *Phys. Rev. B* **65**, 081304(R) (2002).

- 23) K. Nishihira, T. Motooka, Phys. Rev. B **66** 233310 (2002).
- 24) A. Mori, J. Chem. Phys. **110**, 8679 (1999).
- 25) S. R. de Groot and P. Mazur, Nonequilibrium Thermodynamics (Dover, Mineola, 1984).
- 26) M. Uwaha and P. Nozières, J. Phys. (France) **46**, 109 (1985).
- 27) L. Liu, S. Nakano, and K. Kakimoto, J. Cryst. Growth **282**, 49 (2005).
- 28) N. Kobayashi and T. Arizumi, Jpn. J. Appl. Phys. **9**, 361 (1970).
- 29) Y. T. Chan, H. J. Gibling, and H. L. Grubin, J. Appl. Phys. **64**, 1425 (1988).
- 30) M. Li, Y. Li, N. Imaishi, and T. Tsukada, J. Cryst. Growth **234**, 32 (2002).
- 31) V. V. Kalaev, I. Y. Evstratov, and Y. N. Makarov, J. Cryst. Growth **249**, 87 (2003).
- 32) L. Liu, and K. Kakimoto, Int. J. Heat Mass Transfer **48**, 4481 (2005).
- 33) T. Jung, J. Seebeck, and J. Friedrich, J. Cryst. Growth **368**, 72 (2013).