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## Critical Radius for Nucleation

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**CRITICAL RADIUS FOR NUCLEATION**

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## CRITICAL RADIUS FOR NUCLEATION

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### ABSTRACT

The free energy of formation and the critical radius for homogeneous nucleation of a spherical nucleus in supercooled liquid, at given temperature and ambient pressure, are determined, taking fully into account surface area, curvature, and pressure effects. We allow the specific heats and densities of the two phases to be different and all thermophysical properties to be temperature dependent. In the simple case in which classical nucleation theory is valid, our results predict a critical radius of about 40% larger than the classical value, and an activation energy barrier of almost three times larger than the classical value.

#### 1. Introduction

The Gibbs free energy,  $\Delta G$ , of formation of a crystal nucleus in supercooled liquid is the most important quantity in nucleation theory. Several other relevant parameters, such as critical radius, activation energy barrier and frequency of nucleation can be derived from it and some of these are very sensitive to changes in  $\Delta G$  (Chalmers [1], Porter-Earterling [2], Kurz-Fisher [3]). Yet, in classical nucleation theory expressions for  $\Delta G$  are derived under rather gross simplifications (some stated explicitly and some only implicitly assumed) disregarding all but temperature and surface area effects. Since our understanding of nucleation strongly depends on theory, due to the inherent difficulty in experimental observation, it is particularly important that the theory not leave out possibly significant effects.

In this spirit, we determine the free energy of formation of a nucleus at specified supercooling and ambient pressure, taking fully into account surface area, curvature and pres-

sure effects. We allow the specific heats and densities of the two phases to be different and all thermophysical properties to be functions of the appropriate thermodynamic variables. When, for the sake of obtaining explicit expressions, we make restrictive assumptions on thermophysical properties, we state them explicitly.

The inclusion of pressure and interface (surface area and curvature) contributions to the free energy necessitates the derivation of generalized Clapeyron-type equations for the pressure surfaces (because the classical Clapeyron equation is valid only for a flat interface). These are presented in an Appendix in order to make the paper self-contained.

In section 3, we obtain formulae for the critical radius and the corresponding activation energy barrier for the formation of a spherical nucleus. They contain all the effects mentioned above and they can be compared to the classical values ([1], [2], [3]) when the specific heats and the densities of solid and liquid are assumed equal to each other. We find that our critical radius is larger by the factor  $\frac{17}{12} \approx 1.4$  and the critical energy by the factor  $(\frac{17}{12})^3 \approx 2.8$ . The discrepancy arises because the interfacial part of the free energy in the classical theory consists of just  $\gamma A$  instead of  $\gamma\{V\kappa + (A - A_0)\}$ , where  $\gamma$  = interfacial free energy,  $A$  = surface area,  $V$  = volume,  $\kappa$  = mean curvature of the nucleus and  $A_0$  = corresponding area for flat interface. The term  $V\gamma\kappa$  arises from the pressure difference  $P^S - P^L$  via the Laplace relation, and the term  $\gamma(A - A_0)$  arises from the consistent use of reference states (see section 2.4). Hence, for a spherical nucleus, instead of  $\gamma \cdot 4\pi R^2$  we have  $\gamma \cdot \{\frac{4}{3}\pi R^3 \cdot \frac{2}{R} + (4\pi R^2 - \pi R^2)\} = \gamma \cdot \frac{17}{3}\pi R^2$  (when  $\rho^L = \rho^S$ , otherwise there are more correction terms, see section 2.3).

## 2. Free Energies

Consider a pure liquid of density  $\rho^L$  occupying a volume  $V_0$  at temperature  $T$  and pressure  $P^L$ . We assume that the liquid is supercooled, that is,  $T$  is lower than the equilibrium temperature at which liquid and solid with a planar interface can coexist in

equilibrium at the pressure  $P^L$ . Inside this volume consider a small mass  $m$  of liquid which is transforming into a spherical solid nucleus of radius  $R$  at temperature  $T$ , lying in liquid of ambient pressure  $P^L$ . The *free energy of formation* of the solid from liquid is

$$\Delta G = G^S - G^L = m(g^S - g^L)$$

where  $g^L$  is the specific Gibbs free energy of liquid, and  $g^S$  that of solid including the interface. We determine each one separately.

### 2.1. Free Energy of Liquid

We consider (supercooled) liquid of mass  $m$ , at temperature  $T$  and pressure  $P^L$ . Hence

$$dg^L(T, P^L) = -s^L dT + v^L dP^L,$$

with  $s^L$  = specific entropy,  $v^L$  = specific volume =  $1/\rho^L$ . As reference state we choose liquid at  $(T_m, P_{atm})$ , where  $T_m$  is the normal solidification temperature at atmospheric pressure  $P_{atm}$ . Integrating to  $(T, P^L)$  we find

$$g^L(T, P^L) = g^L(T_m, P_{atm}) - \int_{T_m}^T s^L(\bar{T}, P_{atm}) d\bar{T} + \int_{P_{atm}}^{P^L} v^L(T, p) dp. \quad (2.1)$$

The temperature dependence of  $s^L$  is given by

$$s^L(T, P_{atm}) = s^L(T_m, P_{atm}) + \int_{T_m}^T \frac{c_p^L(\tau)}{\tau} d\tau, \quad (2.2)$$

with  $c_p^L(T)$  the specific heat at constant pressure (equal to  $P_{atm}$ ).

For example, if the density  $\rho^L$ , (hence also  $v^L = \frac{1}{\rho^L}$ ), and  $c_p^L$  are constants then we obtain

$$\begin{aligned} g^L(T, P^L) = & g^L(T_m, P_{atm}) - s^L(T_m, P_{atm}) \cdot [T - T_m] \\ & - c_p^L \left[ T \ln \frac{T}{T_m} + (T_m - T) \right] + v^L \cdot [P^L - P_{atm}]. \end{aligned} \quad (2.3)$$

## 2.2. Free Energy of Solid and Interface

Now we consider the same mass  $m$  after it has transformed into a solid nucleus of surface area  $A$  and curvature  $\kappa$  at temperature  $T$ . The solid nucleus will coexist with liquid of pressure  $P^L$ , so according to the Laplace-Young relation (see (A5) in the Appendix) the solid pressure,  $P^S$ , must be higher than  $P^L$  in order to balance the surface tension. Let  $\gamma$  denote the interfacial free energy per unit area and  $a = A/m$  the surface area per gram of solid. Then the specific free energy of the solid is a function of  $T$ ,  $P^S$ ,  $a$  and  $\kappa$ , whose differential is given by (see (A4) in the Appendix)

$$dg^S = -s^S dT + v^S dP^S + \gamma da. \quad (2.4)$$

For simplicity, we have already dropped the curvature terms (see (A3) in the Appendix) because they do not contribute anything for a spherical nucleus. The general case can be found in [4]. Note, however, that curvature effects are still present in (2.4). Indeed, since the solid at state  $(T, P^S)$  must coexist with liquid at state  $(T, P^L)$ , the pressures have to satisfy the Laplace relation (A5) and the generalized Clapeyron equations (A9-A10) derived in the Appendix. Thus  $P^S$  is a function of the remaining thermodynamic variables  $T$ ,  $a$ , and  $\kappa$ . Replacing  $dP^S$  from (A10), (2.4) becomes

$$dg^S = \left\{ -s^S + \frac{v^S}{\Delta v} \Delta s \right\} dT + \left\{ \frac{v^S}{\Delta v} + 1 \right\} \gamma da + \frac{v^L v^S}{\Delta v} d(\gamma \kappa), \quad (2.5)$$

where  $\Delta s = s^L - s^S$  is the specific entropy of fusion and  $\Delta v = v^L - v^S$  is the difference of specific volumes. Of course, the above are valid only for  $\Delta v \neq 0$ ; the special case  $v^L = v^S$  is considered in section 2.4. Replacing the last term by  $d\left(\frac{v^L v^S}{\Delta v} \gamma \kappa\right) - \gamma \kappa \cdot d\left(\frac{v^L v^S}{\Delta v}\right)$ , we have

$$\begin{aligned} d \left[ g^S - \frac{v^L v^S}{\Delta v} \gamma \kappa \right] &= \left\{ -s^S + \frac{v^S}{\Delta v} \Delta s - \gamma \kappa \frac{\partial}{\partial T} \left[ \frac{v^L v^S}{\Delta v} \right] \right\} dT \\ &+ \left\{ \frac{v^L}{\Delta v} \gamma - \gamma \kappa \frac{\partial}{\partial a} \left[ \frac{v^L v^S}{\Delta v} \right] \right\} da. \end{aligned} \quad (2.6)$$

Now we integrate from the state  $(T_m, P_{atm}, a = a_0, \kappa = 0)$ , namely, solid with *planar* interface at  $(T_m, P_{atm})$ , to any state  $(T, a, \kappa)$  to obtain

$$g^S(T, a, \kappa) - \frac{v^L v^S}{\Delta v} \gamma \kappa = g^S(T_m, a_0, 0) - 0$$

$$+ \int_{T_m}^T \left[ -s^S + \frac{v^S}{\Delta v} \Delta s - 0 \right] \Big|_{\substack{a=a_0 \\ \kappa=0}} d\bar{T}$$

$$+ \int_{a_0}^a \left[ \frac{v^L}{\Delta v} \gamma - 0 \right] \Big|_{\kappa=0} da .$$

Using a subscript 0 to denote evaluation at  $a = a_0, \kappa = 0$ , we have

$$g^S(T, a, \kappa) = g_0^S(T_m) + \frac{v^L v^S}{\Delta v} \gamma \kappa$$

$$+ \int_{T_m}^T \left[ -s_0^S + \frac{v_0^S}{\Delta v_0} \Delta s_0 \right] d\bar{T}$$

$$+ \int_{a_0}^a \frac{v^L}{\Delta v} \gamma \Big|_{\kappa=0} da .$$
(2.7)

Note that the temperature dependence of the entropies  $s_0^S$  and  $\Delta s_0$  is similar to (2.2), namely,

$$\Delta s_0(T) = \Delta s_0(T_m) + \int_{T_m}^T \frac{\Delta c_{p0}(\tau)}{\tau} d\tau .$$
(2.8)

where  $\Delta c_p = c_p^L - c_p^S$  is the difference of specific heats.

### 2.3. Free Energy of Nucleus Formation

From (2.1) and (2.7) we find the specific free energy of formation of (spherical) solid of specific area  $a$  of curvature  $\kappa$  to be

$$\begin{aligned}
 \Delta g &= g^S - g^L \\
 &= g_0^S(T_m) - g_0^L(T_m, P_{atm}) \\
 &+ \int_{T_m}^T \left[ 1 + \frac{v_0^S}{\Delta v_0} \right] \Delta s_0 d\bar{T} + \frac{v^L v^S}{\Delta v} \gamma \kappa \\
 &+ \int_{a_0}^a \frac{v^L}{\Delta v} \gamma \Big|_{\kappa=0} d\bar{a} - \int_{P_{atm}}^{P^L} v^L(T, P) dP .
 \end{aligned} \tag{2.9}$$

Now at  $(T_m, P_{atm})$ , solid with planar interface is in equilibrium with liquid, and therefore the free energies  $g_0^S$  and  $g_0^L$  are equal. Substituting  $\Delta s_0$  from (2.8) this becomes

$$\begin{aligned}
 \Delta g &= \int_{T_m}^T \frac{v_0^L}{\Delta v_0} \left[ \Delta s_0(T_m) + \int_{T_m}^{\bar{T}} \frac{\Delta c_{p_0}(\tau)}{\tau} d\tau \right] d\bar{T} - \int_{P_{atm}}^{P^L} v^L(T, P) dP \\
 &+ \frac{v^L v^S}{\Delta v} \gamma \kappa + \int_{a_0}^a \frac{v^L}{\Delta v} \gamma \Big|_{\kappa=0} d\bar{a} .
 \end{aligned} \tag{2.10}$$

The specific volumes and the surface tension coefficient may be considered independent of surface area, so that the last integral is simply  $\frac{v^L}{\Delta v} \gamma (a - a_0)$ . Also, the entropy of fusion at  $T_m$  is simply the latent heat per gram divided by  $T_m$ ,  $\Delta s_0(T_m) = L/T_m$ . If complete thermodynamic data for the material under consideration are available,  $v^i(T, P)$ ,  $i = L, S$  and  $\Delta c_p(T, P_{atm})$  will also be known and therefore all the integrals in (2.10) can be evaluated in terms of data. Of course, very little data is typically available in this supercooled regime and we refer to [5] where several reasonable approximations for  $\Delta c_p$  are discussed. Regarding  $v^i(T, P)$ , it is reasonable to neglect thermal expansion and compressibility so that  $v^L$  and  $v^S$  will be constants. Therefore, under the assumptions

$$\left. \begin{aligned}
 &v^L, v^S \text{ are constants, } v^L \neq v^S, \\
 &\gamma \text{ is independent of surface area}
 \end{aligned} \right\} \tag{2.11}$$

(note that  $\gamma$  may still depend on  $T$  and  $\kappa$ ), we obtain the expression

$$\Delta g = \frac{v^L}{\Delta v} \left\{ -\frac{L}{T_m} \Delta T + F(\Delta c_p, \Delta T) - \Delta v [P^L - P_{atm}] \right\} + \gamma \frac{v^L}{\Delta v} \{v^s \kappa + (a - a_0)\}, \quad (2.12)$$

where  $\Delta T = T_m - T$  is the degree of supercooling at which the nucleus forms,  $L$  is the latent heat of fusion per gram, and

$$F(\Delta c_p, \Delta T) = \int_{T_m}^T \left[ \int_{T_m}^{\bar{T}} \frac{\Delta c_p(\tau)}{\tau} d\tau \right] d\bar{T} \quad (2.13)$$

is a function of  $\Delta c_p(T, P_{atm})$  and  $\Delta T$  only (see [5]).

For a spherical nucleus of radius  $R$ , the transforming mass is

$$m = \frac{4}{3} \pi R^3 \frac{1}{v^s},$$

the mean curvature is  $\kappa = \frac{2}{R}$ , the surface area is  $A = 4\pi R^2$  and the corresponding flat area is  $A_0 = \pi R^2$ . Hence, its free energy of formation at supercooling  $\Delta T = T_m - T$  in liquid of ambient pressure  $P^L$  is given by

$$\begin{aligned} \Delta G(R, T, P^L) &= m \Delta g \\ &= \frac{4}{3} \pi R^3 \frac{v^L}{v^s \Delta v} \left\{ -\frac{L}{T_m} \Delta T + F(\Delta c_p, \Delta T) - \Delta v [P^L - P_{atm}] \right\} \\ &\quad + \gamma \frac{v^L}{\Delta v} \left\{ \frac{4}{3} \pi R^3 \frac{2}{R} + (4\pi R^2 - \pi R^2) \right\}. \end{aligned}$$

or

$$\begin{aligned} \Delta G(R, T, P^L) &= \frac{4}{3} \pi \frac{v^L}{v^s \Delta v} \left\{ -\frac{L}{T_m} \Delta T + F(\Delta c_p, \Delta T) - \Delta v [P^L - P_{atm}] \right\} \cdot R^3 \\ &\quad + \gamma \frac{v^L}{\Delta v} \frac{17}{3} \pi \cdot R^2. \end{aligned} \quad (2.14)$$

This clearly exhibits the effects of  $\Delta v \neq 0$ ,  $\Delta c_p$ ,  $P^L \neq P_{atm}$  and surface tension. The complementary special case  $\Delta v = 0$  will be considered next and comparisons with classical nucleation theory will be made.

#### 2.4. The Special Case $\rho^L = \rho^S$

In the special case of a material with common liquid and solid density, hence

$$v^L = v^S = \text{constant} =: v \quad (2.15)$$

the development is much simpler. Now (2.4) can be written as

$$d[g^S - vP^S] = -s^S dT + \gamma da .$$

Integrating from solid at  $(T_m, a = a_0, \kappa = 0)$  to any  $(T, a, \kappa)$  we obtain

$$\begin{aligned} g^S(T, a, \kappa) &= g^S(T_m, a_0, 0) + v [P^S(T, a, \kappa) - P^S(T_m, a_0, 0)] \\ &\quad - \int_{T_m}^T s^S d\bar{T} + \int_{a_0}^a \gamma |_{\kappa=0} d\bar{a} , \end{aligned} \quad (2.16)$$

which is the analogue of (2.7) for this case. Note that for flat interface at  $T_m$ , we have  $P^L = P^S = P_{atm}$  and  $g^S = g^L$ .

Subtracting (2.1) from (2.15) we find

$$\Delta g = \int_{T_m}^T \Delta s_0 d\bar{T} + v [P^S(T, a, \kappa) - P^L] + \int_{a_0}^a \gamma |_{\kappa=0} d\bar{a} ,$$

which, thanks to the Laplace-Young formula (A5), becomes

$$\Delta g = \int_{T_m}^T \Delta s_0 d\bar{T} + v \gamma \kappa + \int_{a_0}^a \gamma |_{\kappa=0} d\bar{a} . \quad (2.17)$$

As in (2.11), assuming  $\gamma$  independent of  $a$ , and using (2.8), we arrive at

$$\Delta g = \left\{ -\frac{L}{T_m} \Delta T + F(\Delta c_p, \Delta T) \right\} + \gamma \{v \kappa + (a - a_0)\} , \quad (2.18)$$

with  $F(\Delta c_p, \Delta T)$  as in (2.13), which is analogous to (2.12).

The expression in the first bracket, which comes from the entropy of fusion, agrees with classical nucleation theory ([3], p. 25; [2], p. 187), but the second bracket contains two terms that do not appear in the classical theory. One is the curvature term,  $\gamma v \kappa$ ,

which arose from the pressure effect via the Laplace-Young relation and the second is the flat area term,  $-\gamma a_0$ , which arose from the consistent use of reference values.

For a spherical nucleus of radius  $R$ , corresponding to (2.14), we find

$$\Delta G = \frac{4}{3} \pi \frac{1}{v} \left\{ -\frac{L}{T_m} \Delta T + F(\Delta c_p, \Delta T) \right\} \cdot R^3 + \gamma \frac{17}{3} \pi \cdot R^2 . \quad (2.19)$$

Observe that the classical theory produces  $4 \pi$  instead of  $\frac{17}{3} \pi$ .

### 3. Critical Radius of Nucleation

The critical radius,  $R^*$ , is that radius for which the free energy of nucleus formation,  $\Delta G$ , has a local maximum, so that nuclei of radius smaller than  $R^*$  will tend to dissolve and those of radius larger than  $R^*$  will tend to grow.

It follows that at the critical radius

$$\frac{d}{dR} \Delta G \Big|_{R^*} = 0 . \quad (3.1)$$

Applied to (2.14) this yields

$$R^* = \frac{17}{12} \frac{2 \gamma v^S}{\frac{L}{T_m} \Delta T - F(\Delta c_p, \Delta T) + \Delta v [P^L - P_{atm}]} . \quad (3.2)$$

This is seen to be valid even in the special case of section 2.4 by simply setting  $v^L = v^S = v$ .

The corresponding critical value of the free energy of formation (activation energy barrier for homogeneous nucleation) is then given by

$$\Delta G^* = \frac{17^3}{4 \cdot 3^4} \frac{\frac{v^L}{\Delta v} \pi \gamma^3 (v^S)^2}{\left\{ \frac{L}{T_m} \Delta T - F(\Delta c_p, \Delta T) + \Delta v [P^L - P_{atm}] \right\}^2} \quad (3.3)$$

when  $v^L \neq v^S$ , and by

$$\Delta G^* = \frac{17^3}{4 \cdot 3^4} \frac{\pi \gamma^3 v^2}{\left\{ \frac{L}{T_m} \Delta T - F(\Delta c_p, \Delta T) \right\}^2} \quad (3.4)$$

when  $v^L = v^S = v$ .

For heterogeneous nucleation, this must be multiplied by the shape factor ([2], p. 194)

$$S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2/4,$$

where  $\theta$  is the wetting angle.

In classical nucleation theory the approximation  $\Delta c_p = 0$  is usually made and  $v^L = v^S$  is implicitly assumed; the critical radius, obtainable from the usual Gibbs-Thomson relation, has the value ([1], p. 37; [2], p. 189; [3], p. 24)

$$R^*_{\text{classical}} = \frac{2 \gamma T_m}{\rho L \Delta T}$$

and the activation energy barrier has the value ([2], p. 189; [6], p. 377)

$$\Delta G^*_{\text{classical}} = \frac{16 \pi \gamma^3 T_m^2}{3 (\rho L)^2 \Delta T^2}.$$

Taking  $\Delta v = 0$ ,  $\Delta c_p = 0$ , and  $v^S = \frac{1}{\rho}$  in (3.2) and (3.4) we see that

$$R^* = \frac{17}{12} R^*_{\text{classical}} \approx 1.4 R^*_{\text{classical}},$$

and

$$\Delta G^* = \frac{17^3}{4 \cdot 3^4} \frac{3}{16} \Delta G^*_{\text{classical}} \approx 2.8 \Delta G^*_{\text{classical}}.$$

Thus, our critical radius is about 40% larger and the critical energy almost three times larger than the classical values.

## Appendix A

### General Clapeyron-Type Equations in the Presence of Curved Interfaces

Consider a mass  $m$  of a pure material occupying a volume  $V$  and consisting of liquid and solid with masses  $m^L, m^S$ , ( $m^L + m^S = m$ ) volumes  $V_L, V_S$ , ( $V_L + V_S = V$ ), pressures  $P^L, P^S$ , and of interface with surface area  $A$ , and principal curvatures  $\kappa_1, \kappa_2$ . The system is in thermodynamic equilibrium at temperature  $T$ .

The energy changes of such a system are determined by (Adamson [7], p. 59)

$$dU = T dS - P^L dV_L - P^S dV_S + \gamma dA + K_1 d\kappa_1 + K_2 d\kappa_2, \quad (\text{A1})$$

where  $S = S^L + S^S$ ,  $\gamma$  = surface tension, and  $K_1, K_2$  are the coefficients of curvature.

From  $G = U + P^L V_L + P^S V_S - T S$  and (A1) we obtain

$$dG = -S dT + V_L dP^L + V_S dP^S + \gamma dA + K_1 d\kappa_1 + K_2 d\kappa_2 \quad (\text{A2})$$

for the Gibbs free energy  $G(T, P, A, \kappa_1, \kappa_2)$  of the system.

We view the system as consisting of liquid and solid + interface. Thus

$$dG = dG^L + dG^S,$$

where

$$dG^L = -S^L dT + V_L dP^L,$$

$$dG^S = -S^S dT + V_S dP^S + \gamma dA + K_1 d\kappa_1 + K_2 d\kappa_2.$$

Dividing each one by the corresponding mass we obtain the differentials of the specific Gibbs free energies

$$dg^L = -s^L dT + v^L dP^L,$$

$$dg^S = -s^S dT + v^S dP^S + \gamma da + k_1 d\kappa_1 + k_2 d\kappa_2, \quad (\text{A3})$$

where  $s^i$  and  $v^i$  are the specific entropies and volumes,  $a = A/m^S$  is the specific area and  $k_1, k_2$  are the specific coefficients of curvature. Choosing  $k_1 + k_2 = 0$  fixes the interface at the Gibbs "surface of tension" (Adamson [7] p. 60). Then  $k_1 d\kappa_1 + k_2 d\kappa_2 = \frac{1}{2}(k_1 + k_2) d(\kappa_1 + \kappa_2) + \frac{1}{2}(k_1 - k_2) d(\kappa_1 - \kappa_2) = k_1 d(\kappa_1 - \kappa_2)$ , and for a

sphere the contributions from this term will vanish at the end since  $\kappa_1 = \kappa_2 = \frac{1}{R}$ .

Hence, for a spherical interface,  $dg^S$  may be taken simply as

$$dg^S = -s^S dT + v^S dP^S + \gamma da. \quad (\text{A4})$$

The conditions for equilibrium between liquid and solid + interface are the Laplace-Young relation

$$P^S - P^L = \gamma\kappa, \quad (\text{A5})$$

and the equality of free energies

$$g^L(T, P^L) = g^S(T, P^S, a, \kappa). \quad (\text{A6})$$

A discussion on the validity of (A5) and relevant references may be found in [6]. Condition (A6) constrains the pressures to be functions of the remaining independent variables  $T$ ,  $a$ , and  $\kappa$ . We now derive this dependence explicitly, thus obtaining the analogues of the classical Clapeyron equation (which is valid only for planar interfaces).

From (A6), at each coexistence point  $(T, a, \kappa)$  we have

$$dg^L(T, P^L(T, a, \kappa)) = dg^S(T, P^S(T, a, \kappa), a, \kappa).$$

Equating the corresponding partial derivatives and eliminating  $P^S$  via (A5) we obtain after some rearrangements (see [4])

$$d\left[P^L - \frac{v^S}{\Delta v} \gamma\kappa\right] = \frac{\Delta s}{\Delta v} dT + \frac{\gamma}{\Delta v} da - \gamma\kappa d\left(\frac{v^S}{\Delta v}\right), \quad (\text{A7})$$

and then also

$$d\left[P^S - \frac{v^L}{\Delta v} \gamma\kappa\right] = \frac{\Delta s}{\Delta v} dT + \frac{\gamma}{\Delta v} da - \gamma\kappa d\left(\frac{v^L}{\Delta v}\right), \quad (\text{A8})$$

where

$$\Delta s = s^L - s^S, \quad \Delta v = v^L - v^S.$$

Note that the contributions of the curvature differentials vanish for the spherical nucleus case we are considering here. Detailed calculations for the general case (with all the terms retained) appear in Alexiades - Solomon - Wilson [4].

We rewrite (A7) and (A8) in the forms

$$dP^L = \frac{\Delta s}{\Delta v} dT + \frac{\gamma}{\Delta v} da + \frac{v^S}{\Delta v} d(\gamma\kappa). \quad (\text{A9})$$

$$dP^S = \frac{\Delta s}{\Delta v} dT + \frac{\gamma}{\Delta v} da + \frac{v^L}{\Delta v} d(\gamma\kappa). \quad (\text{A10})$$

These are the desired equations, generalizing the classical Clapeyron equation. Indeed, for a flat interface (in which case  $\kappa_1 = \kappa_2$  again, as for a sphere) we have  $\kappa \equiv 0$  and  $a \equiv a_0$ : so only temperature may vary, and  $P^L = P^S$  by (A5). Hence, (A9) and (A10) reduce to the *single* equation

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v}.$$

which is the classical Clapeyron equation ([8]).

The above equations may be integrated to yield generalizations of the expressions in Landau-Lifshitz ([8] p. 523), and then a generalization of the classical Gibbs-Thomson relation may also be derived. We refer the interested reader to Alexiades - Solomon - Wilson [4].

*References*

- [1] B. Chalmers, "Principles of Solidification," Wiley, New York, 1964.
- [2] D. A. Porter and K. E. Easterling, "Phase Transformations in Metals and Alloys," Van Nostrand Reinhold, 1981.
- [3] W. Kurz and D. J. Fisher, "Fundamentals of Solidification," *Trans Tech Publ.*, Switzerland, 1984.
- [4] V. Alexiades, A. D. Solomon and D. G. Wilson, *The Formation of a Solid Nucleus in Supercooled Liquid*, ORNL Report, ORNL/TM-9932, to appear.
- [5] C. V. Thompson and F. Spaepen, "On the Approximation of the Free Energy Change on Crystalization," *Acta Metall.*, **27** (1979), 1855-1859.
- [6] M. Grant and J. D. Gunton, "Theory for the Nucleation of a Crystalline Droplet from the Melt," *Phys. Review B*, **32** (11) (December 1985), 7299-7307.
- [7] A. W. Adamson, "Physical Chemistry of Surfaces," Fourth Edition, Wiley, N.Y., 1982.
- [8] L. D. Landau and E. M. Lifshitz, "Statistical Physics," Part 1, Third Edition, Pergamon Press, Oxford, 1980.

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