

Towards the Theory of Phase Transformations in Metastable Melts: the Phase Transition Temperature Shift

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Abstract. The theory of nucleation and evolution of particles in supercooled and supersaturated liquids is developed taking into account the Gibbs-Thomson effect and the attachment kinetics of atoms at the growing solid/liquid surfaces. An exact analytical solution of model equations is constructed in a parametric form. The Gibbs-Thomson effect essentially influences a dynamic behavior of liquid metastability and distribution function.

INTRODUCTION

The phenomena of crystal nucleation and growth from supersaturated solutions and supercooled melts are the basis of various technological processes in the chemical and food industries, and also form the basis for the production of different drugs [1-9]. The dynamics of phase transition processes in metastable liquids depends on many factors that determine the state and characteristics of the system, which, for example, include kinetics of nucleation and crystal growth, the intensity of liquid desupersaturation/desupercooling, and initial conditions [10-14]. These factors manifest themselves to one degree or another at all stages of the phase transformation, which include the initial, intermediate, and final stages of the process. At the initial stage, supersaturation/supercooling is large, which leads to the beginning of the process of crystal nucleation. This stage transforms into the intermediate one, when nucleation and crystal growth occur simultaneously and, as a result, desupersaturation/desupercooling takes place (see, among others, [15-18]). The intermediate stage, in turn, goes to the final stage, when there are a lot of crystals and they begin to interact with each other due to the processes of Ostwald ripening and coagulation [19-25].

In the present paper, we consider the evolution of particulate ensembles at the intermediate stage with allowance for the nonlinear growth rates of individual crystals caused by the Gibbs-Thomson effect and the attachment kinetics of atoms at the solid/liquid surfaces of evolving spherical particles.

GOVERNING EQUATIONS

Let us analyze a time behavior of macroscopically homogeneous one-component metastable liquid (supercooled melt or supersaturated solution) filled with nucleating and growing solid particles. The dynamics of such particles is defined by the kinetic equation for the crystal-radius distribution function $f(r, \tau)$, where r and τ represent the particle radius and time. This equation reads as

$$\frac{\partial f}{\partial \tau} + \frac{\partial}{\partial r}(gf) = \frac{\partial}{\partial r}\left(D\frac{\partial f}{\partial r}\right), \quad r > r_*, \quad \tau > 0, \quad (1)$$

where r_* stands for the critical radius of particles, i.e. the particles are unstable and vanish if $r < r_*$ while they are unstable and evolve if $r > r_*$. Here $g = dr/d\tau$ is the growth velocity of particles, and D is the coefficient of mutual Brownian diffusion.

The heat balance equation for the liquid supercooling $\Delta\theta$ takes the form [10]

$$\Delta\theta = \Delta\theta_0 - b\Delta\theta_0 \int_{r_*}^{\infty} r^3 f(r, \tau) dr, \quad \tau > 0, \quad (2)$$

where $\Delta\theta_0$ is the initial supercooling, $b = 4\pi L_V / (3\rho_m C_m \Delta\theta_0)$, ρ_m and C_m represent the density and specific heat of the mixture, and L_V is the latent heat parameter.

For the sake of definiteness, we chose the following initial and boundary conditions

$$f = 0, \Delta\theta = \Delta\theta_0, \tau = 0, \quad (3)$$

$$f \rightarrow 0, r \rightarrow \infty; \frac{dr}{d\tau} f - D \frac{\partial f}{\partial r} = I(\Delta\theta), r = r_*, \quad (4)$$

where $I(\Delta\theta)$ represents the rate of nucleation. In the case of Weber-Volmer-Frenkel-Zel'dovich (WVfZ) and Meirs (M) kinetic mechanisms, the nucleation rate reads [26]

$$I_{\text{WVfZ}} = I_* \exp\left(-\frac{p\Delta\theta_0^2}{\Delta\theta^2}\right), I_{\text{M}} = I_*(\Delta\theta)^p, \quad (5)$$

where I_* and p are assumed to be constant.

The growth rate of each crystal depends on the supercooling $\Delta\theta = \theta_p - \theta_l$ (θ_p and θ_l are the phase transition temperature and temperature far from the crystal), interface curvature $1/r$ and the attachment kinetics of atoms at the solid/liquid interface (the contribution inversly proportional to the kinetic coefficient μ) [27-29]

$$\frac{dr}{d\tau} = \beta_* \left(\theta_p - \theta - \frac{\chi}{r} - \frac{1}{\mu} \frac{dr}{d\tau} \right) = -\frac{\lambda_l}{L_V} \frac{\partial \theta}{\partial \rho}, \rho = r(\tau), \quad (6)$$

where β_* is the growth rate kinetic coefficient, ρ is the spherical coordinate, $\chi = \theta_p \alpha / L_V$ (α is the coefficient of surface tension), θ is the temperature field around the growing crystal, and λ_l is the temperature conductivity coefficient. To find the growth rate $dr/d\tau$, we use the temperature conductivity equation and the boundary condition far from the crystal, i.e.

$$\nabla^2 \theta = 0, \rho > r(\tau); \theta \rightarrow \theta_l, \rho \gg r(\tau). \quad (7)$$

The growth rate following from the solution of the boundary-value problem (6), (7) takes the form

$$\frac{dr}{d\tau} = \frac{\tilde{\beta}_* (\Delta\theta - \chi/r)}{1 + \tilde{\beta}_* q_T r}, \quad (8)$$

where $\tilde{\beta}_* = \beta_* \mu / (\beta_* + \mu)$ and $q_T = L_V / \lambda_l$. The model equations (1)-(5) and (8) represent the integro-differential problem for the determination of the distribution function $f(r, \tau)$ and liquid supercooling $\Delta\theta(\tau)$. Below we extend the previously developed theory [16] to include the Gibbs-Thomson effect (temperature shift caused by the interface curvature, χ/r in (6)) and the attachment kinetics (temperature shift $\mu^{-1} dr/d\tau$ in (6)).

Note that if we are dealing with the supersaturated solutions, $\Delta\theta$ and $\Delta\theta_0$ should be respectively replaced by the current and initial supersaturations ΔC and ΔC_0 , and $b = 4\pi C_p / 3\Delta C_0$, where C_p represents the concentration at saturation [16-26]

ANALYTICAL SOLUTIONS

For the sake of simplicity, let us use the dimensionless parameters of the form [16]

$$\begin{aligned} w &= \frac{\Delta\theta}{\Delta\theta_0}, F = l_0^4 f, s = \frac{r}{l_0}, t = \frac{\tau}{\tau_0}, s_* = \frac{r_*}{l_0}, I_0 = I(\Delta\theta_0), \sigma = \frac{\chi}{l_0 \Delta\theta_0}, g_0 = \frac{\tau_0 g}{l_0}, \\ \tau_0 &= \left(\tilde{\beta}_*^3 \Delta\theta_0^3 I_0 \right)^{-1/4}, l_0 = \left(\frac{\tilde{\beta}_* \Delta\theta_0}{I_0} \right)^{1/4}, u_0 = \frac{d_0}{l_0}, D = \frac{d_0 g}{R}, R = \frac{r - r_*}{l_0}, Q = \tilde{\beta}_* q_T l_0, \\ z &= s - s_*, d_0 = \frac{k_B \theta}{8\pi \alpha l_0}, x_1 = \int_0^t g_0(\tilde{t}) R(l_0 s(\tilde{t})) d\tilde{t}, z_1 = \int_0^z R_1(\tilde{z}) d\tilde{z}, R_1(z) = R(l_0(z + s_*)). \end{aligned} \quad (9)$$

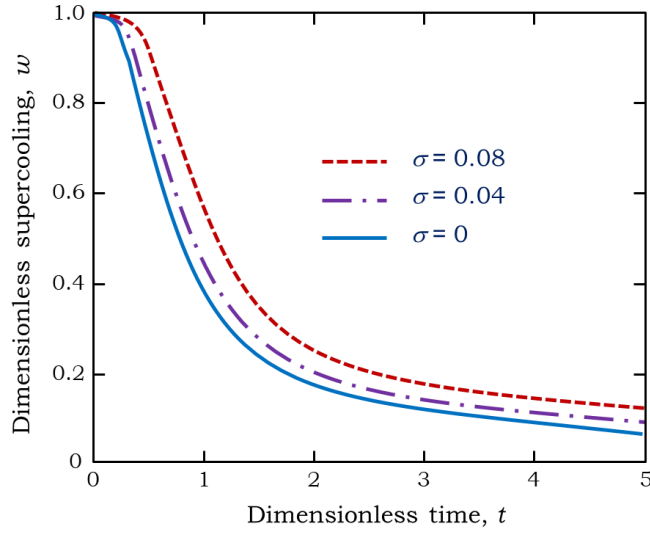


FIGURE 1. Supercooling versus time.

The solution of model (1)-(5), (8) written out in dimensionless form using designations (10) for the Meirs kinetic mechanism becomes [16]

$$F(x_1, z_1(s)) = I_0^4 f = \int_0^{x_1} J(x_1 - y_1) \gamma(y_1, z_1) dy_1, \quad J(x_1) = \frac{w^p [1 + Q(s_* + \sqrt{2x_1})]}{w(x_1) - \frac{\sigma}{s_* + \sqrt{2x_1}}},$$

$$t(x_1) = \int_0^{x_1} \frac{1 + Q(s_* + \sqrt{2\tilde{x}_1})}{\sqrt{2\tilde{x}_1} \left[w(\tilde{x}_1) - \frac{\sigma}{s_* + \sqrt{2\tilde{x}_1}} \right]} d\tilde{x}_1, \quad h(y_1) = \int_0^\infty \frac{(s_* + \sqrt{2\tilde{z}_1})^3 \gamma(y_1, \tilde{z}_1)}{\sqrt{2\tilde{z}_1}} d\tilde{z}_1, \quad (10)$$

$$(1 + Qs_*)H(x_1)(2-p)(1-p) = (w^{2-p})(1-p) - \frac{\sigma}{s_*} (w^{1-p} - 1)(2-p), \quad p \neq 1, \quad p \neq 2,$$

$$(1 + Qs_*)H(x_1) = w - 1 - \frac{\sigma}{s_*} \ln w, \quad p = 1, \quad (11)$$

$$(1 + Qs_*)H(x_1) = \ln w + \frac{\sigma}{s_*} \left(\frac{1}{w} - 1 \right), \quad p = 2,$$

$$\gamma(y_1, z_1) = \frac{1}{2u_0} \exp\left(\frac{2z_1 - y_1}{4u_0}\right) \left[\frac{2\sqrt{u_0}}{\sqrt{\pi y_1}} \exp\left(\frac{-z_1^2}{4u_0 y_1}\right) - \exp\left(\frac{z_1}{2u_0} + \frac{y_1}{4u_0}\right) \operatorname{erfc}\left(\frac{z_1}{2\sqrt{u_0 y_1}} + \frac{\sqrt{y_1}}{2\sqrt{u_0}}\right) \right],$$

$$H(x_1) = -b \int_0^{x_1} h(y_1) dy_1. \quad (12)$$

Expressions (10)–(12) determine the exact analytical solutions of the problem under consideration in a parametric form (where the modified time x_1 plays the role of this parameter) with allowance for the Gibbs-Thomson effect and the attachment kinetics of atoms at the growing solid-liquid interfaces of particles. As this takes place, expressions (11) represent implicit equations for the determination of liquid supercooling w .

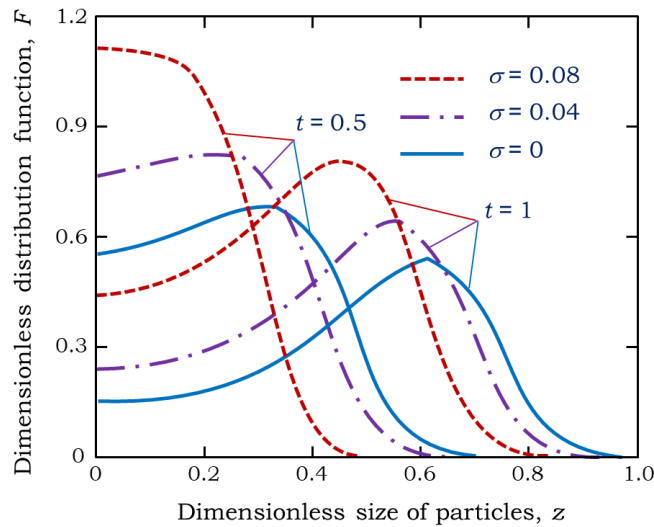


FIGURE 2. Distribution function versus time.

CONCLUDING REMARKS

Figures 1 and 2 illustrate a behavior of analytical solutions (10) and (12); physical parameters are given in [16]. As easily seen, the metastability degree (dimensionless supercooling w) decreases with time, because growing crystals release the latent heat of crystallization, and compensates the system metastability. As this takes place, the Gibbs-Thomson effect shifts the curves to larger supercooling at each fixed time t (figure 1). This is explained by the fact that the crystal growth rate (8) becomes slower with increasing $\chi \sim \sigma$. Figure 2 demonstrates that the particle-radius distribution function increases, attains a maximum value and decreases with increasing the size z of particles. As this takes place, this function becomes a bell-shaped with increasing the time of crystallization. The Gibbs-Thomson effect essentially shifts the distribution function. Taking this effect into account, we see that all curves move to the left (in the direction of smaller sizes) and their maximum points increase. This occurs due to larger supercooling with increasing σ and, as a consequence, due to more intensive nucleation and crystal growth processes.

The theory under consideration can be extended to the case of simultaneous consideration of the bulk and directional crystallization with a mushy layer, where nucleation of crystals and the growth of solid phase can occur. Such a theory can be developed on the basis of the recent approach and previously elaborated theories of directional crystallization [30-38].

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