

Supporting Material for: Predicting the kinetics of ice recrystallization in aqueous sugar solutions

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Abstract

We review various extensions of LSW theory to finite volume fraction. The respective equations for the averaged volumetric growth rate and its dependence on volume fraction are discussed first, followed by a detailed derivation of the equations for the stationary particle-size distribution (PSD) and coarsening rate.

1 Extending LSW theory to finite volume fraction

1.1 Averaged volumetric growth rate

A common method to relax the LSW assumption of zero dispersed-phase volume fraction is to consider the growth of a particle in the centre of a spherical cell of finite size instead of an infinite medium. Denoting the radius of the cell as a_c , the (Laplacian) composition gradient

at the surface of a particle is now obtained as

$$\left. \frac{\partial x_i^\alpha(r)}{\partial r} \right|_{r=a} = \frac{x_i^\alpha(a_c) - x_i^\alpha(a)}{a(1 - a/a_c)} \quad (1)$$

As for the LSW theory, the particles are assumed to interact with the averaged composition of the matrix phase, but now at a distance a_c instead of infinity. The corresponding averaged volumetric growth rate of particles of size a can be written as a simple modification of the LSW result, according to

$$B(z) = \frac{B^{\text{LSW}}(z)}{1 - z/z_c} \quad (2)$$

Various empirical methods have been proposed for relating the rescaled cell size z_c to the volume fraction of the dispersed phase. Some possibilities are the introduction of some geometrical quantity such as the average distance to nearest neighbours,^{1,2} or the introduction of some constraints satisfying the macroscopic specification of the system under consideration.³⁻⁶ Of these models, the macroscopic model of Marsh and Glicksman⁵ seems to lead to the most accurate comparison to experiments. The most prominent assumption underlying this model is the *Ansatz* that the rescaled cell size scales with the rescaled particle size, according to

$$z_c^3 = Pz^3 + E \quad (3)$$

The constants P and E are obtained by ensuring two global constraints are met: The first constraint ensures a constant dispersed-phase volume fraction (which has been proven to be a valid approximation within the asymptotic limit of long coarsening times⁷), according to

$$\phi_V^\beta = \frac{\langle z^3 \rangle}{\langle z_c^3 \rangle} \quad (4)$$

whereas the second constraint ensures that the average composition of all cells equals the composition at the surface of a particle of critical size a^* , as

$$\frac{\left\langle \frac{B(z)+6}{3z} (z_c^3 - z^3) - \frac{B(z)}{2} (z_c^2 - z^2) \right\rangle}{\langle z_c^3 - z^3 \rangle} = 2 \quad (5)$$

where the angular brackets $\langle \cdot \rangle$ denote averages over the ensemble of particles.

A different approach to include the effect of finite dispersed-phase volume fraction on the growth rate is to recast the system of growing and shrinking particles in terms of a system of point sources and sinks of the precipitating species.⁸⁻¹³ In principle this allows for a rigorous statistical-mechanical approach, involving a diagrammatic series expansion in ϕ_V . Due to complexity of the method, however, the series has only been developed up to first order. Assuming a random spatial arrangement of particles, Marqusee and Ross (MR) derived⁹

$$B(z) = [1 + z/z_s] B^{\text{LSW}}(z) \quad (6)$$

where

$$z_s = \sqrt{\frac{\langle z^3 \rangle}{3\phi_V \langle z \rangle}} \quad (7)$$

is a dimensionless screening length. Related approaches not restricted by the absence of spatial correlations between particles have been developed, but at a price of increased complexity.^{8,10} Since the MR approach is only a first order theory, its application is expected to be limited to low volume fractions.

A similar theory expected to be more useful for application to intermediate volume fractions, is that of Brailsford and Wynblatt.¹⁴ Their model assumes the particles to grow or shrink within a field of homogeneous source-sink strength. By introducing a spherical cavity of radius a_c containing a particle of radius $a < a_c$ in the system (with $\phi_V = a^3/a_c^3$ and $\nabla^2 x^\alpha(r) = 0$ for $a < r < a_c$), and deriving the flux of material into the cavity, a self-consistent theory for the size- and volume-fraction dependent growth rate could be developed. Using

an (approximate) interpolation formula between the self-consistent results for $\phi_V = 0$ and $\phi_V = 1$, the averaged growth rate could be approximated to the same form as Eq. (6), with a screening length

$$z_s = \frac{2 \langle z^3 \rangle}{3\phi_V \langle z^2 \rangle + \sqrt{9(\phi_V \langle z^2 \rangle)^2 + 12\phi_V \langle z^3 \rangle \langle z \rangle}} \quad (8)$$

The growth rates of Eqs. (2)-(8) clearly show that, compared to LSW theory, all theories for finite dispersed-phase volume fraction suffer from the additional difficulty that the averaged growth rate $B(z)$ depends on certain statistical averages $\langle \cdot \rangle$ over the ensemble of particles. In other words, the averaged growth rate is a functional of the PSD, the correct notation for which would be $B[f_{\text{eq}}(z); z]$. Due to the functional dependence, calculation of growth rates cannot be uncoupled from the calculation of the stationary PSD, which complicates the analysis. In the next section we derive the respective equations.

1.2 Stationary PSD and coarsening rate

For deriving the stationary PSD, it is instructive to switch to the particle volume $V = a^3$ and rescaled particle volume $v = V/V^*(t)$ as variables. Rewriting the continuity equation in terms of the rescaled particle volume v , one obtains

$$\frac{\partial n(v, t)}{\partial t} + \frac{\partial n(v, t) \dot{v}}{\partial v} = 0 \quad (9)$$

with

$$\dot{v} = \frac{B[f_{\text{eq}}(v); v] - vK^*}{V^*(t)} \quad (10)$$

and

$$K^* \equiv \frac{da^{*3}}{dt} \quad (11)$$

the coarsening rate of the critical particle size. Introducing the condition for self-similarity

$$n(v, t) = f_{\text{eq}}(v)n(t) \quad (12)$$

leads to reformulation of the continuity equation to the following partial differential equation

$$(B[f_{\text{eq}}(v); v] - vK^*) \frac{1}{f_{\text{eq}}(v)} \frac{df_{\text{eq}}(v)}{dv} + \left(\frac{dB[f_{\text{eq}}(v); v]}{dv} - K^* \right) + V^*(t) \frac{1}{n(t)} \frac{dn(t)}{dt} = 0 \quad (13)$$

The statistical-self-similarity hypothesis of Mullins¹⁵ shows that, *if* a stationary PSD exists, the coarsening rate K^* must be a constant. Under this condition, the first two terms of the above equation depend only on v , whereas the third term depends only on t , leading to the following two ordinary differential equations

$$(B[f_{\text{eq}}(v); v] - vK^*) \frac{1}{f_{\text{eq}}(v)} \frac{df_{\text{eq}}(v)}{dv} + \left(\frac{dB[f_{\text{eq}}(v); v]}{dv} - K^* \right) = \lambda \quad (14)$$

$$-V^*(t) \frac{1}{n(t)} \frac{dn(t)}{dt} = \lambda \quad (15)$$

where λ is a separation constant. The value of λ is obtained from the condition that, for long coarsening times (asymptotic limit), the volume fraction of dispersed phase material will tend to a constant (see the work of Marqusee and Ross⁷ for a justification of such an approach). Using Eq. (12), one obtains

$$\phi_V = V^*(t)n(t) \int_0^\infty f_{\text{eq}}(v)v dv \quad (16)$$

which leads to the insight that, in the asymptotic limit,

$$n(t)V^*(t) = \text{constant} \quad (17)$$

Using this in Eq. (15), one obtains

$$\lambda = K^* \quad (18)$$

Substitution in Eq. (14), followed by a separation of variables, leads to the following general solution for the stationary PSD

$$f_{\text{eq}}(v) = \frac{C}{B[f_{\text{eq}}(v); v] - vK^*} \exp \left[\int_0^v \frac{K}{B[f_{\text{eq}}(v'); v'] - v'K^*} dv' \right] \quad (19)$$

The normalisation constant C is obtained by ensuring the PSD integrates to unity. Under the condition that $f(v)$ vanishes for rescaled volumes beyond a certain cut-off, one finds

$$C = -\lambda \quad (20)$$

Rewriting in terms of the rescaled particle radius $z = a/a^*(t)$, we obtain

$$f_{\text{eq}}(z) = \frac{-3z^2K^*}{B[f_{\text{eq}}(z); z] - z^3K^*} \exp \left[\int_0^z \frac{3z'^2K^*}{B[f_{\text{eq}}(z'); z'] - (z')^3K^*} dz' \right] \quad (21)$$

which, due to the functional dependence of the growth rate on the PSD, is an implicit equation. For the LSW theory, this equation is explicit.

The vanishing of the PSD for rescaled particle sizes above a certain maximum value z_m was first shown by LSW, who derived the following stability criterion based on a mass balance constraint for the precipitating species

$$f_{\text{eq}}(z > z_m) = 0 \quad (22)$$

$$\left. \frac{\partial z}{\partial t} \right|_{z_m} = 0 \quad (23)$$

$$\left. \frac{\partial}{\partial z} \frac{\partial z}{\partial t} \right|_{z_m} = 0 \quad (24)$$

The stability argument can be rewritten in terms of the volumetric growth rate $B[f_{\text{eq}}(z); z]$, leading to a set of equations that can be solved for the coarsening rate K^* (which so far was

undetermined), according to

$$z_m = \frac{3B[f_{\text{eq}}(z_m); z_m]}{\left. \frac{dB[f_{\text{eq}}(z); z]}{dz} \right|_{z_m}} \quad (25)$$

$$K^* = \frac{B[f_{\text{eq}}(z_m); z_m]}{z_m^3} \quad (26)$$

For the growth rate used in the LSW theory, Eqs. (25)-(26) are explicit, and can be solved analytically, as

$$z_m^{\text{LSW}} = \frac{3}{2} \quad (27)$$

$$K^{*\text{LSW}} = \frac{8}{9}\xi \quad (28)$$

when substituted in Eq. (21), this leads to the famous LSW result

$$f_{\text{eq}}^{\text{LSW}}(z) = \frac{4}{9}z^2 \left(\frac{3}{3+z} \right)^{7/3} \left(\frac{3/2}{3/2-z} \right)^{11/3} \exp \left(\frac{z}{z-3/2} \right) \quad (29)$$

For any of the extensions of LSW theory to finite volume fraction, the coarsening rate and PSD can only be calculated by solving the combined set of Eqs. (21) and (25)-(26), using an iterative routine. The LSW distribution Eq. (29) can be used as an initial guess. For the Marsh and Glicksman model there is an additional difficulty, as the iterative procedure needs to be performed under the constraints of Eqs. (3)-(5), which require an additional, nested, iterative procedure. In this case, the initial guess for the PSD is determined by the initial guess for the model parameters P and E of Eq. (3).

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