Lattice Boltzmann model for crystal growth from supersaturated solution

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[1] We develop a new, lattice effects-free lattice Boltzmann model for simulating crystal growth from supersaturated solution. Simulations of crystal growth from a single or multiple nuclei in a domain initially filled with supersaturated solution are presented, such as in the case of gas hydrate formation. We find that as the process changes from diffusion-controlled to surface reaction-controlled, the crystal transforms from open cluster-type structure, via compact coral-type structure, to compact circular structure, and correspondingly, the fractal dimension of the crystal structure increases from a value close to that of a diffusion-limited aggregation (DLA) structure to the Euclidian value for a circle. At a high Damkohler number, crystal formed from a single nucleus becomes more compact as the saturation increases. At a low Damkohler number, the crystal has a fairly round shape for different saturation values and the effect of saturation is insignificant. *INDEX TERMS:* 1010 Geochemistry: Chemical evolution; 3210 Mathematical Geophysics: Modeling; 3250 Mathematical Geophysics: Fractals and multifractals; 3620 Mineralogy and Petrology: Crystal chemistry. **Citation:** Kang, Q., D. Zhang, P. C. Lichtner, and I. N. Tsimpanogiannis (2004), Lattice Boltzmann model for crystal growth from supersaturated solution, *Geophys. Res. Lett.*, *31*, L21604, doi:10.1029/2004GL021107.

1. Introduction

[2] The past decade has seen great advances in lattice gas automata (LGA) and lattice Boltzmann (LB) methods as powerful numerical tools for simulating complex fluid flows and modeling physics in fluids. Unlike conventional numerical schemes based on discretizations of macroscopic continuum equations, the LGA and LB methods are based on microscopic models and mesoscopic kinetic equations. This feature gives the LGA and LB methods the advantage of studying non-equilibrium dynamics, especially in fluid flow applications involving interfacial dynamics and complex boundaries (geometries). Since their appearance, they have been successfully applied to studying a variety of flow and transport phenomena such as flow in porous media, turbulence, multiphase and multicomponent flows, particles suspended in fluids, and heat transfer and reaction-diffusion [*Chen and Doolen*, 1998]. Compared to these applications, there are relatively few studies using the LB method to study

crystal growth. Only recently two thermal LB methods with enhanced collisions and coupled with phase-field method have been adapted to the problem of liquid-solid phase transition [*de Fabritiis et al.*, 1998; *Miller et al.*, 2001].

[3] In this letter, we develop a simple reaction model for isothermal crystal growth from a supersaturated solution in the context of the LB method with a Bhatnagar-Gross-Krook (BGK) collision operator [*Qian et al.*, 1992; *Chen et al.*, 1992]. The use of the lattice BGK model makes the computations more efficient and allows the flexibility of varying transport coefficients.

[4] This work is the first step towards the numerical study of formation and decomposition of gas hydrates. Gas hydrates are crystalline, non-stoichiometric, clathrate compounds. They are formed by certain gases (such as methane, ethane, and carbon dioxide) when contacted with water under low temperature and high pressure. The physical properties of these compounds give rise to numerous applications in the broad areas of energy production and storage and climate effects [*Sloan*, 2003]. The largest challenge in hydrate research is to describe the kinetics of hydrate formation and decomposition. It has been theoretically demonstrated and experimentally observed that hydrate formation is not restricted to a thin layer close to the gas-liquid interface but can occur anywhere in the liquid water phase if the solution is supersaturated [*Tohidi et al.*, 2001]. However, the formation mechanism is still not fully understood, especially in porous media.

[5] Even though there is not a unified hydrate kinetics model yet, it is important to perform a set of sensitivity studies on the control parameters based on the existing kinetics models. In this work, we numerically simulate crystal growth from a supersaturated solution with the LB model. We perform a set of parametric studies varying the Damkohler number (a parameter that describes the effect of reaction relative to that of diffusion) and saturation using a first-order kinetic rate law and examine the effects of these parameters on the patterns of crystal growth.

2. Lattice Boltzmann Method

[6] In the current study, we ignore the thermal effects and assume that the solute concentration does not affect the density and velocity of the solution. The solute transport in such a system can be described by the following lattice BGK equation:

$$g_i(\mathbf{x} + \mathbf{e}_i\delta_t, t + \delta_t) = g_i(\mathbf{x}, t) - [g_i(\mathbf{x}, t) - g_i^{eq}(C, \mathbf{u})]/\tau_s, \quad (1)$$

where g_i is the distribution function of the solute concentration, δ_t is the time increment, τ_s is the relaxation time, C and $\mathbf{u}$ are the solute concentration and the fluid velocity, respectively, $\mathbf{e}_i's$ are the discrete velocities, and g_i^{eq}

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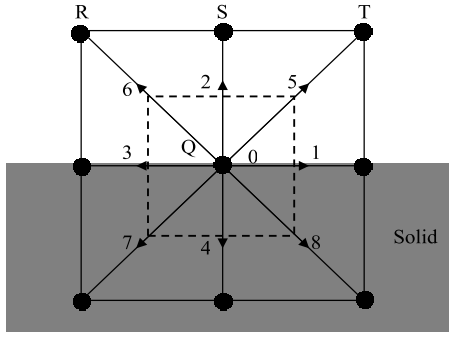
Figure 1. Schematic illustration of a wall node.

is the corresponding equilibrium distribution function. In the most commonly used two-dimensional, nine-speed (D2Q9) model, $\mathbf{e}'_i s$ have the following form:

$$\mathbf{e}_i = \begin{cases} 0 & i = 0, \\ (\cos[(i-1)\pi/2], \sin[(i-1)\pi/2]) & i = 1-4, \\ \sqrt{2}(\cos[(i-5)\pi/2 + \pi/4], \sin[(i-5)\pi/2 + \pi/4]) & i = 5-8, \end{cases} \quad (2)$$

τ_s is related to the diffusivity by $D = (\tau_s - 0.5)/3$, and g_i^{eq} has the following form:

$$g_i^{eq}(C, \mathbf{u}) = \omega_i C \left[1 + 3\mathbf{e}_i \cdot \mathbf{u} + 4.5(\mathbf{e}_i \cdot \mathbf{u})^2 - 1.5\mathbf{u}^2 \right], \quad (3)$$

where $\omega'_i s$ are the associated weight coefficients, which are $\omega_0 = 4/9$, $\omega_i = 1/9$ for $i = 1, 2, 3, 4$, and $\omega_i = 1/36$ for $i = 5, 6, 7, 8$. The solute concentration is calculated using

$$C(\mathbf{x}, t + \delta_t) = \sum_i g_i(\mathbf{x}, t + \delta_t). \quad (4)$$

Using the Chapman-Enskog expansion technique, one can prove that the above LB equation recovers the following convection-diffusion equation [*Dawson et al.*, 1993]:

$$\partial C/\partial t + (\mathbf{u} \cdot \nabla)C = \nabla \cdot (D\nabla C). \quad (5)$$

[7] Since we have assumed that the solute concentration does not affect the density and velocity of the fluid, we can use the evolution equation of another distribution function to describe the fluid flow. This equation has been shown to recover the correct continuity and momentum equations at the Navier-Stokes level [*Qian et al.*, 1992; *Chen et al.*, 1992]. In previous studies of chemical dissolution and precipitation in porous media, we have shown that the LB method can provide detailed flow information in pore space [*Kang et al.*, 2002, 2003]. In this study, we will focus on the effect of Damkohler number and supersaturation on the crystal growth by ignoring the fluid flow, though the method presented here is equally applicable to the situation where flow is present.

3. Boundary Conditions

[8] For generality and simplicity, we consider the general first-order kinetic-reaction model at the fluid-solid interface [*Lasaga*, 1981]:

$$D\partial C/\partial n = k_r(C - C_s), \quad (6)$$

where D is the diffusivity, C is the solute concentration at the interface, C_s is the saturation concentration, k_r is the

local reaction-rate constant, and n is the direction normal to the interface pointing toward the fluid phase. This reaction model is very similar to a typical kinetic model for hydrate formation proposed by *Englezos et al.* [1987] and by *Bishnoi and Natarajan* [1996]. The driving force in their model is the difference in the fugacity of the dissolved gas and its fugacity at the three phase equilibrium while it is the concentration difference ($\Delta C = C - C_s$) in our study.

[9] The above formulation describes a boundary condition for solute concentration. In previous studies we have formulated a boundary condition for the distribution function [*Kang et al.*, 2002, 2003]. We have based our approach on the observation that, at a stationary wall, the non-equilibrium portion of the distribution function is proportional to the dot product of the function's microscopic velocity and the concentration gradient. Figure 1 is a schematic illustration of a wall node. After each streaming process of the particle distribution function (g_i), g_0, g_1, g_3, g_4, g_7, and g_8 of node Q are known. In contrast, we must determine g_2, g_5, and g_6, using the boundary conditions. To determine the solute concentration at this node, we use the known distribution function g_4:

$$C = (g_4 + \beta C_s)/(\omega_4 + \beta), \quad (7)$$

where $\beta = k_r/(8D)$ [*Kang et al.*, 2002, 2003]. On the basis of C and $\mathbf{u}$, we can calculate g_i^{eq} from equation (3). From this result we then can calculate the unknown distribution functions: $g_2 = g_2^{eq} + g_4^{eq} - g_4$; $g_5 = g_5^{eq} + g_7^{eq} - g_7$; and $g_6 = g_6^{eq} + g_8^{eq} - g_8$.

[10] We neglect the solute diffusion in the solid and assume that crystal growth only occurs at liquid-solid interface. Each node at the interface represents a control volume with a size of 1×1 (in lattice units) and is located at the center of this volume. As we can see from Figure 1, node Q is the center of the control volume surrounded by dashed lines. Initially, this control volume is given a mass b_0. We update the mass at every time step by $b = b + \Delta x k_r (C - C_s)\delta t = b + k_r(C - C_s)$, where Δx is the length of the control volume along the interface and δt is the time increment. Both of them equal unity in this case. For this control volume, when $b = 2b_0$, i.e., when the mass doubles, one of the nearest (S) or diagonal liquid nodes (R and T) becomes a solid particle with a probability of $P_S = 4P_R = 4P_T$. The ratio of solidification probability between the nearest node and diagonal nodes is 4:1, which equals the ratio of weight coefficients between the vertical ($\mathbf{e}_2$) and diagonal directions ($\mathbf{e}_5$ and $\mathbf{e}_6$). By doing so, we eliminate the lattice grid effects.

4. Simulation Results and Discussions

[11] The simulation geometry is a two-dimensional cell of size $h \times h$, where h equals 200 (in lattice units) in this study. Initially, the domain is filled with a supersaturated solution with a concentration C_0. At time zero, a stable nucleus is introduced at the center of the domain. Crystal begins to grow subsequently. Simple dimensional analysis suggests that there are two important dimensionless parameters, which control the processes. They are the relative concentration or saturation ($\psi = \frac{C_0}{C_s}$) and Damkohler number (Da). The Da number is defined as $\frac{k_r h}{D}$ and describes the effect of reaction relative to that of diffusion.

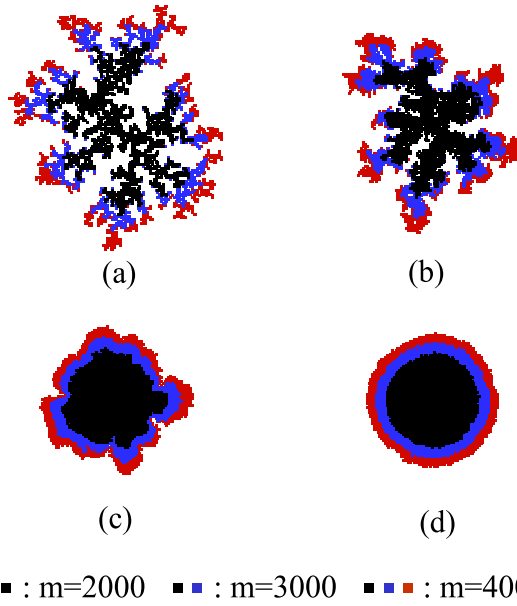**: m=2000** ■ : m=2000　■■ : m=3000　■■■ : m=4000

Figure 2. Crystal structures developed at different Da numbers and at solute saturation 1.2: (a) $Da = 600$; (b) $Da = 150$; (c) $Da = 48$; (d) $Da = 2$.

[12] Figure 2 shows crystal structures at different Da numbers and at 2000, 3000, and 4000 solid particles (crystal mass). The solute saturation is 1.2. As we can see from (a), the crystal is not compact. As the Da number decreases, the process becomes more and more surface reaction-controlled. Compared to the reaction, the mass transfer via diffusion is now fast. The solute can be easily transported from the bulk to the liquid-solid interface located at the center area of the domain. Therefore, the crystal growth is expected to be more compact, centered with the initial nucleus. This result is consistent with that of the multiparticle diffusion-limited aggregation (MPDLA) simulation of solidification structures of alloy melt, in which the morphology transforms from open cluster-type structures, via compact coral-type structures, to compact facetted structures as the process changes from diffusion-controlled to interface kinetics-controlled [*Das and Mittemeijer*, 2001]. In addition, the crystal shape in case (d) is a fairly round shape if we take into account the randomness introduced in the growth. This indicates that our model is free of lattice grid effects, which exist in other numerical simulations of crystal growth [*Das and Mittemeijer*, 2001; *Xiao et al.*, 1988]. In their studies, the final crystal shape depends on the lattice used in the numerical simulation, even for the case of isotropic growth.

[13] Table 1 gives the approximate fractal dimension values (D_f) for the crystal structure at different Da numbers. Calculations are based on 30 realizations and a maximum of 4000 crystal particles for each case. As can be seen, D_f decreases from about 2 (the Euclidian dimension of a circle) to 1.75 (only 2.3% greater than 1.71, the fractal dimension

Table 1. Fractal Dimension Values

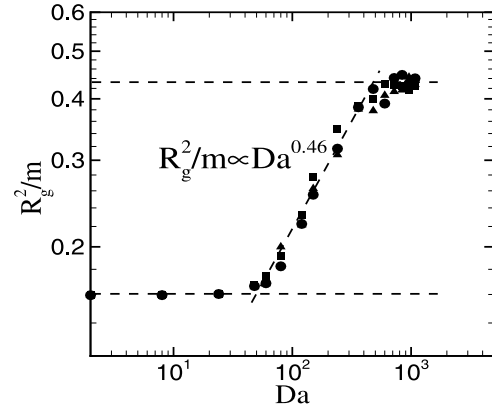| Da	2	48	96	150	600
D_f	2.002 ± 0.001	1.95 ± 0.01	1.80 ± 0.02	1.77 ± 0.02	1.75 ± 0.02

Figure 3. The square of radius of gyration of the crystal (normalized by the crystal mass) at different Da numbers and at solute saturation 1.2. Different symbols indicate different realizations.

of a DLA structure [*Feder*, 1988]) as Da number increases from 2 to 600. A more accurate estimate of D_f needs more realizations and particles and hence requires much longer computational time.

[14] Figure 3 shows the dependence of the square of radius of gyration of the crystal (normalized by the crystal mass) on Da number at solute saturation 1.2 and 3000 solid particles. The radius of gyration indicates the compactness of the crystal [*Feder*, 1988]. It is clear that as the Da number increases, the radius increases too, showing a decrease of the compactness of the crystal structure. The radius has two asymptotic values at a very small and a very large Da number, respectively, and varies according to a power law at Da number values in between. Results from different realizations agree with each other very well at small Da numbers, but deviate as the Da number becomes large. This is so because the small Da number corresponds to a surface reaction-controlled process and different realizations result in almost the same compact round-shape structure. For a large Da number, however, different realizations may result in very different but statistically similar structures.

[15] Figure 4 shows the dependence of the square of the radius of gyration of the crystal at equilibrium state and at
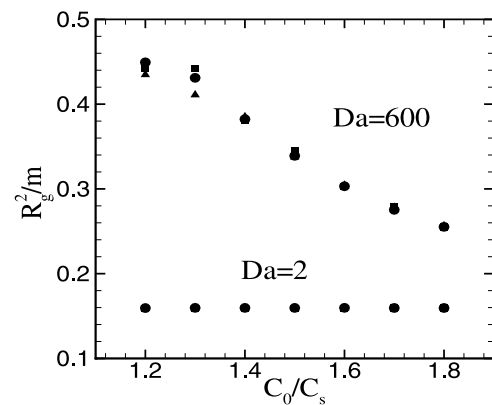

Figure 4. The square of radius of gyration of the crystal (normalized by crystal mass) at different saturation and Da numbers. Different symbols indicate different realizations.
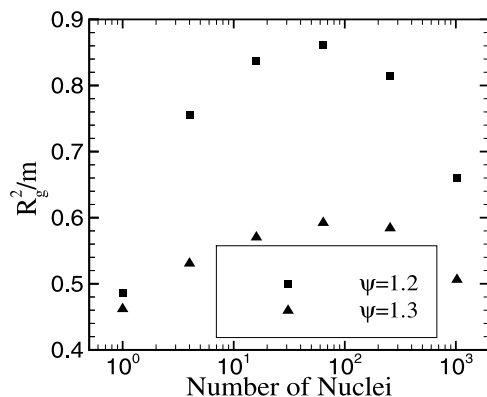
Figure 5. Dependence of the square of the radius of gyration of crystal clusters (normalized by the total mass of the crystal clusters) at equilibrium state on the number of initial nuclei at saturation 1.2 and 1.3.

different Da numbers on the initial saturation. It is clear that at a large Da number, the radius decreases as the saturation increases. This is so because there is only one initial nucleus in the system and growth can only occur at the liquid-solid interface. Therefore, a high degree of supersaturation makes it easier for the solute to transport to the interface and hence the process is more like a reaction-controlled one. The effect of saturation becomes insignificant at a very small Da number because the process is already reaction-controlled. Since this observation is relative to each single nucleus, it may be different from experimental observations. Because in the hydrate-formation experiments, the supersaturation may cause the formation of multiple nuclei in the system, hydrate may grow from each individual of these nuclei, resulting in incompact overall hydrate structures.

[16] To demonstrate this, we have performed a set of simulations of crystal growth from multiple initial nuclei. Since the mechanism of hydrate nucleation is still not understood and needs to be experimentally studied [*Bishnoi and Natarajan*, 1996], we assume that the initial stable nuclei are uniformly distributed in the domain. Figure 5 shows the dependence of the square of the radius of gyration (normalized by the total mass of the crystal clusters) on the number of initial nuclei at saturation 1.2 and 1.3. As can be seen, although the radius for the single nucleus at $\psi = 1.2$ is greater than its counterpart at $\psi = 1.3$, it is smaller than those for multiple nuclei at $\psi = 1.3$. Since it is likely that the higher saturation may cause the formation of more initial nuclei in the system, the final crystal clusters of the system with higher saturation may be less compact than those of the system with lower initial saturation. For both saturations, the radius increases with the number of initial nuclei at first, and then decreases as the number becomes so large that interaction between clusters from different nuclei tends to make the clusters in the system more compact.

5. Conclusions

[17] We have developed a new, lattice effects-free lattice Boltzmann model for simulating crystal growth from supersaturated solution and applied it to the simulations of crystal growth from a single or multiple nuclei in a domain initially filled with supersaturated solution. We found that as the process changes from diffusion-controlled to surface reaction-controlled, the crystal transforms from open cluster-type structure, via compact coral-type structure, to compact circular structure, and correspondingly, the fractal dimension of the crystal structure increases from a value close to that of a diffusion-limited aggregation (DLA) structure to the Euclidian value for a circle. At a high Damkohler number, crystal formed from a single nucleus becomes more compact as the saturation increases. At a low Damkohler number, the crystal has a fairly round shape for different saturation values and the effect of saturation is insignificant.

[18] As pointed out above, even though there is no flow in these simulations, the method presented here is equally applicable to crystal growth scenarios where flow exists. Simulation results of crystal growth with fluid flow will be presented in another publication. Finally, we would like to point out that the crystal growth is a moving-boundary problem, even for the pure diffusion case presented here. By implementing the kinetic-reaction model into the boundary conditions of the LB model and by tracking the mass accumulation in each control volume at the interface, this method takes full advantage of the kinetic nature inherent in the LB method and avoids solving a moving-boundary problem [*Bekri et al.*, 1997], or using a phase-field method to define the solid and liquid fraction [*Miller et al.*, 2001]. It also differs from the Monte Carlo method where an attempt for an atom to deposit at the interface or return back to the liquid is implemented by comparing the solidification and melting probabilities with two random numbers [*Das and Mittemeijer*, 2001]. The randomness in our method only exists in the solidification step where it is necessary to determine in which direction the solid particles will grow. However, whether this randomness reflects the reality is a subject of more careful studies. Also the new findings like the effect of saturation need to be verified from experimental studies of formation kinetics of hydrate.

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