Profile decay by surface diffusion at low temperature

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(Received 19 November 1993)

We describe an efficient Monte Carlo simulation of profile decay via surface diffusion on a $(1+1)D$ square-lattice system with suppressed roughening. Our algorithm takes advantage of analytical results for a one-dimensional random walker and is valid in the low-temperature limit of noninteracting activated walkers. We find that an initially sinusoidal profile decays nonexponentially with a characteristic decay time which increases with the initial amplitude. At a fixed ratio of initial amplitude to wavelength, the decay time τ increases with wavelength λ as $\tau \sim \lambda^{3.5\pm0.1}$. In this model, profile decay arises from irreversible decay of the peak and valley terraces rather than from step-step interactions.

How does a corrugated surface on a crystalline solid relax toward equilibrium? The dominant relaxation mechanism is often surface diffusion. Above the roughening temperature T_r, a continuum picture is appropriate and the surface-mass current is driven by gradients in the surface curvature.[1] The continuum model predicts that corrugations of wavelength λ decay exponentially with a time constant $\tau \sim \lambda^4$, a prediction that has been verified by profile decay experiments on metal surfaces[2,3] at $T > T_r$. At $T < T_r$, corrugated metal surfaces are observed to form facets,[4] but the scaling of the decay time with wavelength has not been established. Monte Carlo simulations[5,6] of profile evolution via surface diffusion at $T < T_r$ have produced a rich array of decay characteristics, but neither clear evidence of faceting nor a simple scaling of the decay time has been observed. These simulations have employed various simplifying assumptions in order to reduce an otherwise intolerable computation time. Analytical efforts to describe smoothing dynamics via surface diffusion at $T < T_r$ include thermodynamic models, which treat the crystal as a continuum,[7,8] and microscopic models, which include the effects of the atomic lattice.[9-11] The microscopic models assume that the profile decay is driven by a long-ranged repulsive step-step interaction due in part to strain fields surrounding atomic steps and in part to configurational entropy due to wandering of the step edge.[12] These microscopic models predict no decay in the absence of such a step-step interaction, in marked contrast to our results. Here we describe a Monte Carlo method to simulate profile decay via surface diffusion at low temperatures in a model system with a one-dimensional (1D) substrate. In this model, the decay is due to an irreversible decay of the peak and valley terraces, rather than step-step repulsion.

The system we consider is a square lattice solid-on-solid model with one substrate dimension and height $(1+1)D$. The surface of a $(1+1)D$ crystal roughens at nonzero temperatures, but, like previous investigators,[9-11] we artificially suppress roughening in order to approximate the smoothing dynamics of a $(2+1)D$ crystal with straight parallel grooves at $T < T_r$. In our $(1+1)D$ model, only kink-site atoms are allowed to activate and become wandering adatoms. Surface atoms not at kink sites are not allowed to activate, and, consequently, roughening of this $(1+1)D$ surface does not occur. We further assume that the temperature is sufficiently low that activated adatoms may be considered noninteracting. In this low-temperature regime, we find that profile decay is nonexponential with a characteristic decay time, which increases with the initial amplitude of the modulation. At a fixed initial amplitude, the decay time τ increases with the wavelength λ as $\tau \sim \lambda^{2.9\pm0.1}$. At a fixed ratio of initial amplitude to wavelength, the decay time increases as $\tau \sim \lambda^{3.5\pm0.1}$. Faceting (or at least extreme surface flattening) is observed, and after an initial transient, the decay of the profile is shape preserving.

We assume first- and second-nearest-neighbor interactions only, so that the potential near a monatomic step has the form shown in Fig. 1(a), with a deep well at the base of the step, shallow wells far from the step, and a barrier-height asymmetry $\Delta \geq 0$. At any temperature $T > 0$, a kink atom trapped in the deep well at the step

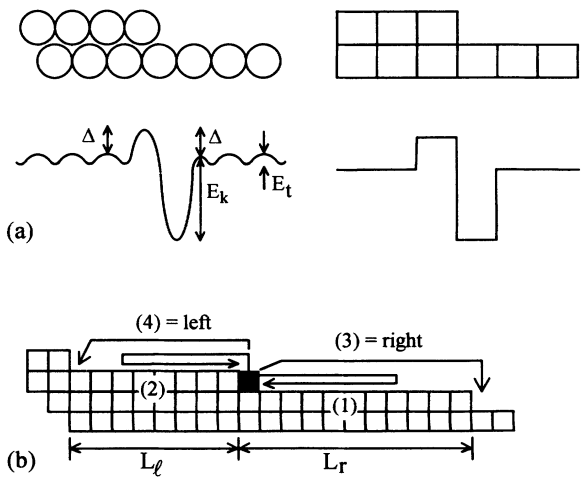

FIG. 1. (a) Step potential for triangular and square lattices. (b) Possible trajectories of an activated kink atom.

will detach after a mean time $\tau_{\rm det}$, and will either activate *out* onto the lower terrace with probability O or *up* onto the upper terrace with probability U, where $O+U=1$. Because of the asymmetry in this potential, $U \leq O$ and $U/O=e^{-\beta\Delta}$, where $\beta=1/(k_BT)$. Also because of the asymmetry, an adatom approaching the step from the left will reflect with a probability k, while an adatom approaching from the right will not reflect and will be captured in the well. The barrier asymmetry Δ, the reflection probability k, and the temperature are related by $k=1-e^{-\beta\Delta}$. Consequently, U, O, and k are related by $U/O=1-k$.

An important difference between this $(1+1)D$ model and the corresponding $(2+1)D$ model is the absence of long-ranged interactions between steps in $(1+1)D$. In a $(2+1)D$ cubic-lattice model, step ledge wandering due to kinks arrayed along the step ledge (into the page in Fig. 1) leads to an effective entropic repulsion between step ledges, even in the absence of direct energetic interactions. However, this degree of freedom and its entropy are absent in the $(1+1)D$ model.

In a real metal, the terrace corrugation E_t [Fig. 1(a)] is small compared to the kink-well depth E_k, and so the time for an adatom to random walk across a terrace is fast compared to the mean time for a kink atom to detach. As a result, at low temperatures, the rate-limiting step in mass flow is the detachment of kink atoms and there is rarely more than one adatom on a terrace at any time. The condition that the random-walk time is much less than the kink-detachment time is $L^2e^{\beta E_t} \ll e^{\beta E_k}$, where L is the terrace width in units of the lattice constant. Thus, the regime of noninteracting walkers is $k_BT<(E_k-E_t)/(2\ln L)\cong E_k/(2\ln L)$. Taking $L\approx 10-100$ leads to $k_BT<E_k/10$. For low-index Ni surfaces, $E_k\approx 0.7-0.8$ eV,[13] and the low-temperature regime is approximately $T<\frac{1}{2}T_{\rm melting}$.

The basic idea behind our simulation is that, instead of simulating the entire random walk between the initial and final positions of an activated walker, one can move the atom directly to the final site with the appropriate probability and then advance the time by an amount proportional to $\tau_{\rm det}$. Consider the behavior of an atom at a kink site on the stepped surface of a square lattice as shown in Fig. 1(b). When the atom detaches from the kink site, it will execute one of four trajectories: (1) Activation onto the lower terrace, followed by an unbiased random walk, and after zero, one, or more reflections at the step down $(x=+L_r)$, a final return to the home kink site. (2) Activation onto the upper terrace and after a random walk and some reflections at the home step $(x=0)$, a final transmission through the barrier, and a return to the home kink site. (3) Activation onto the lower terrace, some reflections at $x=+L_r$, a hop down to the next lower terrace, and capture at the lower step. (4) Activation onto the upper terrace, a meandering walk and some reflections at $x=0$, and a final capture at the upper step at $x=-L_l$. Trajectories (1) and (2) result in no surface current, (3) results in a "downhill" rightward mass flow, and (4) results in an "uphill" leftward flow. The problem of an unbiased random walker in 1D surrounded by

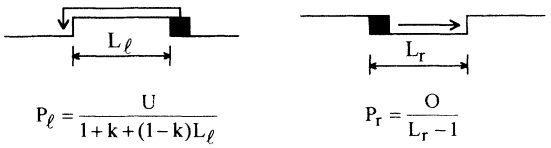

FIG. 2. Kink environments and probabilities of motion on the top and bottom terraces.

reflecting or absorbing barriers can be solved exactly.[14] Defining $\eta_l=1-(1/L_l)$ and $\eta_r=1-(1/L_r)$, we find for the probabilities of the four trajectories (see the Appendix),

$$P_1=O\frac{\eta_r(1-k)+k(1-\eta_r)}{(1-\eta_r k)}\ ,\quad P_2=U\frac{\eta_l(1-k)}{(1-\eta_l k)}\ ,$$
$$P_r=\frac{O}{L_r}\frac{(1-k)}{(1-\eta_r k)}\ ,\quad P_l=\frac{U}{L_l}\frac{1}{(1-\eta_l k)}\ , \tag{1}$$

where k is the probability of reflection from a step down, P_1 is the probability of process (1), P_r is the probability of rightward process (3), etc. For the special case of terraces of equal width $(L_r=L_l)$, the step-potential condition $(U/O=1-k)$ leads immediately to $P_r=P_l$. In this case, the reflection coefficient k just cancels the tendency toward "downhill" flow and there is no net surface current. However, when terraces have unequal width, the balance is broken and there is a net mass flow toward the direction of higher step density.

Kinks on the top and bottom terraces of a corrugated surface have different environments than those on the sloping hillsides and have different movement probabilities, as shown in Fig. 2. We argue that the behavior of the top and bottom terraces is essential for profile decay in this model. Because of the condition of noninteracting adatoms, island nucleation is forbidden, and so when a top terrace completely decays, it can never reform. Furthermore, because nonkink atoms are not allowed to activate, the bottom terrace of atoms, once filled, can never empty. Thus, over time, the top terrace acts as a net source of walkers and the bottom terrace acts as a sink, resulting in profile decay even though the hillsides have no bias toward downhill flow.

We first describe the details of the simulation when the surface modulation consists of monatomic steps separated by wide terraces. We will then discuss how the simulation is modified to include steeply sloped surfaces with

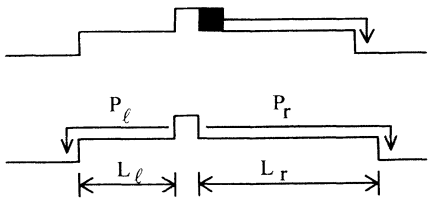

FIG. 3. An abandoned adatom on a top terrace.

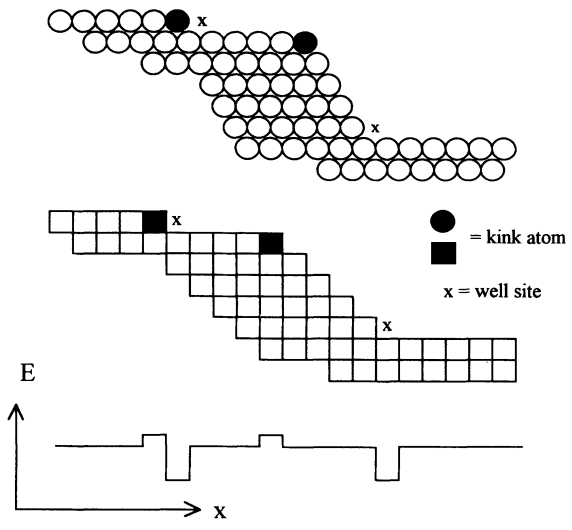

FIG. 4. Surfaces of the triangular and square lattices and the corresponding surface potential.

closely spaced steps. The evolution of our square-lattice system is entirely determined by the initial surface profile and the single input parameter k, which is a measure of the temperature or the barrier asymmetry. The equations $U/O=1-k$ and $U+O=1$ allow one to eliminate U and O in favor of k: $O=1/(2-k)$, $U=(1-k)/(2-k)$. The probabilities that a particular kink atom will move to the adjacent right or left step upon activation depend on the environment of the kink, that is, the distances L_r and L_l to the steps on the right and left and whether those steps are up or down. Our simulation begins with a listing of the N kink sites, their environments, and their probabilities P_r and P_l for right and left movement. Next, a kink is chosen at random from the list and that kink either moves to the right with probability P_r, or it moves to the left with probability P_l, or it remains unmoved with probability $P_1+P_2=1-(P_r+P_l)$. Regardless of the movement, the time is advanced by an amount $\tau_{\rm det}/N$ which is the mean time between successive kink detachment events in the whole system. If the kink atom does move, the local topology and possibly the number N of kinks are changed. The list of kink sites, their environments, and the movement probabilities are then updated, another kink atom is chosen at random from the list, and the cycle repeats.

When the top terrace on a hill is reduced to two atoms, movement of either atom down the hill results in a remaining single adatom which, in a real system, would immediately random walk until it is captured by a step (Fig. 3). Our simulation checks for abandoned adatoms after every hop and moves the adatom to the right or left step down with the probabilities appropriate for a random walker between reflective barriers,

$$P_r=\frac{1+L_l(1-k)}{2+(L_r+L_l)(1-k)}\ ,\quad P_l=1-P_r\ , \tag{2}$$

where, as in Fig. 3, L_r and L_l are the distances to the right and left steps.

In a simulation of this type, one must decide how to handle the interaction of steps when the terrace width is small. We have decided to make the sloped (11) face of the square-lattice stable and equivalent to the flat (10) face. Adatoms are allowed to wander freely on both the (10) and (11) surfaces. Surface atoms of the (11) face are not kink atoms and are not allowed to detach. In this way, our square lattice system accurately mimics the expected behavior of a triangular lattice. As shown in Fig. 4, the flat and sloped surfaces of a faceted triangular lattice are equivalent, and an adatom should random walk on the two surfaces in an identical manner. In the triangular lattice, kink atoms are those with exactly three nearest neighbors (NN's), while in the square lattice we define kink atoms at those with exactly two first NN's (one below and one to the side) and two second NN's (both below). Wandering adatoms are captured at the *well sites,* marked with ×'s in Fig. 4. In a triangular lat-

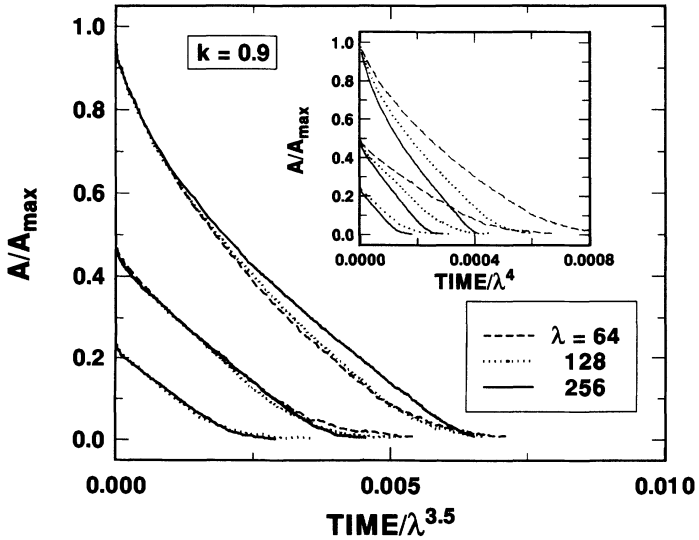

FIG. 5. Mean scaled amplitude vs scaled time for systems at $k=0.9$. $A_{\rm max}=\lambda/(2\pi)$ is the maximum possible initial amplitude consistent with monatomic steps.

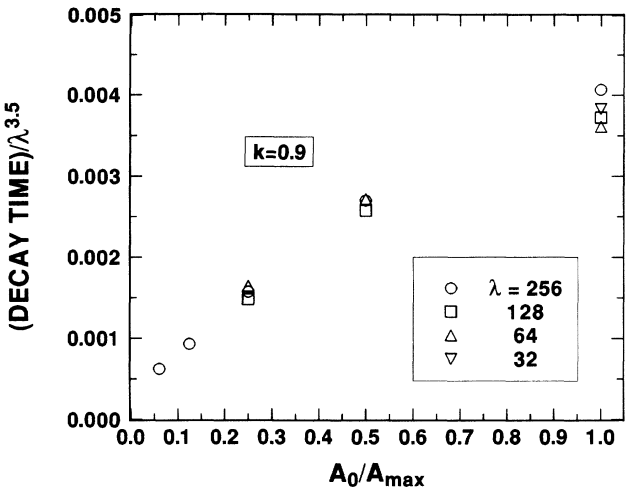

FIG. 6. Scaled decay time vs scaled initial amplitude $A_0/A_{\max}$. The decay time is the time to decay to $\frac{1}{4}$ of the initial amplitude measured in units of the mean kink-detachment time.

tice, a well site is an empty surface site with exactly three first NN's; in the square lattice, a well site is one with exactly two first NN's (one below and one to the side) and two second NN's (both below). With these definitions of kink atoms and well sites, the (11) face of the square lattice is equivalent to the sloped face of the triangular lattice. Both possess a kink atom and a reflective barrier at the top edge, and both possess a well, but no kink, at the bottom edge. On a square-lattice surface with both (10) and (11) faces, kink atoms detach and wander to adjacent wells, rather than to adjacent steps, and we must consider how to alter the probabilities P_r and P_l of right and left motion. A surface with monatomic steps separating (10) terraces always has reflective barriers attached to well sites, while a surface with both (10) and (11) faces has some reflective barriers which are separated from well sites, but they still come in pairs. It can be shown that the probability that a kink-site atom will detach and random walk to an adjacent well is independent of the position of a reflective barrier between the initial and final sites. Thus, our modified simulation uses exactly the same probabilities P_r and P_l as before, but with L_r and L_l now interpreted as the distances to adjacent wells, rather than adjacent steps. With this method, double steps and surfaces steeper than the (11) face cannot form.

We now turn to the results of our simulations. The initial profile is a discretized sine wave of wavelength λ and initial amplitude $A_0 < A_{\max} = \lambda/(2\pi)$. Initial amplitudes $A_0 > A_{\max}$ are not allowed since these would result in faces more steeply sloped than the (11) face. Figure 5 is a plot of the mean scaled amplitude $A/A_{\max}$ vs scaled time for various wavelengths and initial amplitudes, all at $k=0.9$, which corresponds to a temperature of $k_B T = 0.434\Delta$. Our system has a substrate of length 8192 with periodic boundary conditions, so the number of wavelengths averaged varies from 128 cycles of $\lambda=64$ to 32 cycles of $\lambda=256$. The unit of time is the mean detachment time τ_{det}. We see that, at fixed ratio of initial amplitude over wavelength, the decay time scales as $\lambda^{3.5\pm0.1}$, a result not previously predicted. A similar plot of absolute amplitude A vs scaled time shows that, at fixed initial amplitude, the decay time scales as $\lambda^{2.9\pm0.1}$, a result predicted in Ref. 10 for 2D (bidirectional) grooves, but not 1D grooves. The decay is nonexponential with a characteristic decay time which increases with the initial amplitude, as shown in Fig. 6, where the decay time is defined as the time for the mean amplitude to fall to $\frac{1}{4}$ of its initial value.

Figure 7 shows the time evolution of the average profile for a system with $\lambda=256$, $A_0 = A_{\max}$, and $k=0.9$. The initial sine-wave profile very quickly evolves to a shape with flattened peaks and valleys. After the initial transient, the profile evolution is shape preserving (inset, Fig. 7), a result also found in the analytical treatment of Ref. 11.

Finally, we return to the question of what drives the profile decay in this simple $(1+1)D$ model. We have ex-

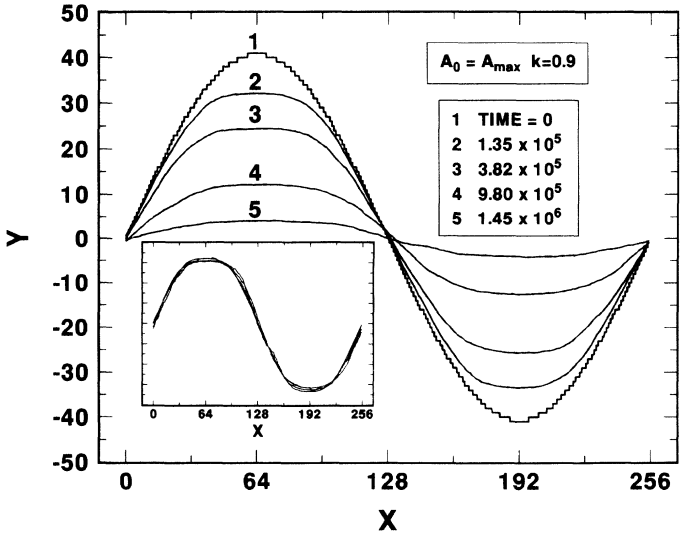

FIG. 7. Time evolution of the mean profile for $\lambda=256$, averaged over 32 wavelengths. The inset displays the profiles scaled to have equal areas, showing that the evolution is shape preserving.

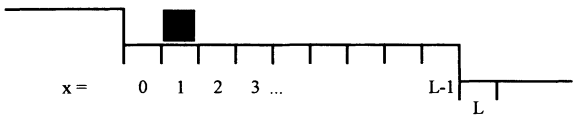

FIG. 8. Coordinate system for an adatom on a terrace of width L.

plored the behavior of our model for various values of k between 0 and 0.99, and we find similar results at all values including $k=0$, which corresponds to no barrier asymmetry. Hence, the decay is not driven by the step-potential asymmetry. Nor is it due to any long-ranged step-step repulsion, which is manifestly absent in our model. Instead, the decay is due to random fluctuations coupled with the irreversible behavior of the top and bottom terraces. Most of the time the system explores configurations with equal numbers of terraces and steps, and hence equal energies and nearly equal entropies, and there is little or no driving force. However, the system occasionally stumbles upon a state of lower free energy when the number of terraces is reduced by one and there are suddenly two less steps in the system. The evidence for these statements is that the sizes of the top and bottom terraces are observed to fluctuate in a random manner. A top terrace W atoms wide requires about W^2 exchanges with the second terrace before it decays to zero length and similarly for the bottom terrace. The system's free energy thus decreases in a discontinuous manner, not like that of a ball rolling down an inclined plane, but like that of a random walker on a terrain consisting of terraces separated by steep cliffs, with the walker occasionally falling down a level. This picture differs qualitatively from previous analytical treatments[9-11] in which step-step repulsion provides a continuous driving force or profile decay. We emphasize that the absence of step-step repulsion is an artificial feature of our $(1+1)D$ model and that in $(2+1)D$ systems step-step repulsion certainly exists due to the entropy of step wandering. However, our simulation demonstrates that such a step-step interaction is not a requirement for profile decay.

We gratefully acknowledge useful conversations with P. M. Duxbury, A. Zangwill, J. Hetherington, E. Capriotti, and L. McCann. This work was supported in part by the NSF under Grant No. DMR-8857364.

APPENDIX

Here we calculate the probability P_r in Eq. (1) for the movement of a kink atom to the adjacent downhill step. The other movement probabilities in Eqs. (1) and (2) are computed similarly. As shown in Fig. 8, we consider an adatom starting at position $x=1$ after having just been activated from position $x=0$ out onto a terrace of width L. The adatom commences an unbiased random walk and completes its walk when it is trapped by one of the two sinks at $x=0$ and L. A partially reflecting barrier with reflection probability k is at the step down between $x=L-1$ and L. This is a Markov process and we can find the probability that the walker is absorbed at $x=L$ by setting up rate equations. In setting up these equations, it is useful to imagine a continuous flow of noninteracting atoms emerging from a source at $x=1$ and then random walking among scattering centers at $x=1,2,\ldots,L-1$ before disappearing at sinks $x=0$ and L. We ask what fraction of atoms are absorbed at $x=L$, in the steady state. Let c be the rate at which atoms are emitted by the source at $x=1$; let N_i be the rate at which atoms arrive at (are scattered from) position $x=i$; and let a_0 and a_L be the rates of absorption at $x=0$ and $x=L$, respectively, so that $c=a_0+a_L$ and a_L/c is the probability of absorption at L. The probability which we seek is then $P_r=O(a_L/c)$ where O is the probability of activation of the kink site atom from $x=0$ to $x=1$. The rate equations for this problem are

$$a_0=\frac{c}{2}+\frac{N_1}{2}\ , \tag{A1}$$

$$N_1=N_2/2\ , \tag{A2}$$

$$N_2=\frac{c}{2}+\frac{N_1}{2}+\frac{N_3}{2}\ , \tag{A3}$$

$$N_3=\frac{N_2}{2}+\frac{N_4}{2}\ ,\ \text{etc.}\ , \tag{A4}$$

$$a_L=\frac{N_{L-1}}{2}(1-k)\ . \tag{A5}$$

From (A1)–(A4), we have $N_1=2a_0-c$, $N_2=4a_0-2c$, $N_3=6a_0-4c$, $N_4=8a_0-6c$, etc., which leads, by induction, to

$$N_i=2ia_0-2(i-1)c\ ,\quad i=2,3,4,\ldots,(L-1)\ . \tag{A6}$$

From (A5) and (A6) we get

$$a_L=(1-k)[(L-1)a_0-(L-2)c]\ . \tag{A7}$$

Using $c=a_0+a_L$ to eliminate a_0 from (A7), we have finally

$$\frac{a_L}{c}=\frac{(1-k)}{1+(1-k)(L-1)}\ . \tag{A8}$$

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