# Anomalous crystal growth of a binary chain

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Crystal growth in a two-component chain is studied by Monte Carlo simulation. The mean displacement $\langle n(t) \rangle$ of the solid-liquid interface is found proportional to the time $t$ in a one-phase region, and to $t^{\nu_1}$ in a two-phase coexistence region with an exponent $\nu_1$ being smaller than 1, and decreasing on leaving the phase boundary. The variance $\sigma(t)$ deviates from the linearity in time at a lower concentration in the one-phase region. This dynamical transition is related to the change of the probability distribution $P(n, t)$. In the one-phase region the peak of $P$ shifts steadily, whereas in the two-phase region $P$ is scaled only by the width. Even though the model has a finite backward jump probability, the obtained behaviors of $\langle n(t) \rangle$, $\sigma(t)$, and $P(n, t)$ agree with those of the one-dimensional random directed walk.

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## I. INTRODUCTION

The growth of a crystal with the control of an atomic level has been one of the major topics of study recently. Understanding of the growth kinetics is also deepened by the development of atomic scale observation techniques such as scanning tunneling microscopy and various electron microscopies. For an alloy crystal, the growth is affected by various factors such as supersaturation, thermal and chemical diffusion, chemical segregation, and interface morphology. At low temperatures when a crystal interface is atomically flat, the crystal growth is controlled solely by interface kinetics.

In an extreme limit, growth may proceed as a one-dimensional motion of a kink site along the step. Temkin has previously introduced a simple one-dimensional model to describe a binary alloy growth [1–3]. A site on a chain is occupied by an $A$ or $B$ atom, which can be in a solid or in a liquid state. The chain is decomposed into two parts by a single interface site; solid is to the left and liquid to the right, for example. The solidification or melting takes place only at this solid-liquid interface position. He has shown exactly that the steady motion of the interface is possible in a one-phase region, but in the two-phase region the velocity of the interface advancement vanishes. Also the concentrations behind and ahead of the interface are exactly shown to take the values of the coexisting solid and liquid phases, respectively, in the two-phase region.

There are a few exactly soluble one-dimensional models which show an anomalous time dependence of the mean displacement [4–6]. The diffusion constant is also known to become anomalous by varying a control parameter [6]. For the random directed walk, exact solution of mean displacement, variance, as well as a scaling form of the probability distribution are also known [7–9]. In the crystal growth of a binary chain there is a finite rate of a back jump. We want to understand the interface motion of this model by the Monte Carlo simulation. We find that the simulation results can be explained completely just by relating the concentration of $B$ atoms, $C$, to the parameter $\mu$ of the random directed walk.

## II. MODEL

The pure $A$ atoms solidify at the equilibrium melting temperature $T_A$ with the specific latent heat $L_A$. At a temperature $T$ near $T_A$, the chemical potential difference of an $A$ atom in the liquid and the solid states is approximately written as $\mu_A = (L_A/T_A)(T_A - T)$. The corresponding values are described similarly for $B$ atoms. As for the mixture of $A$ and $B$ atoms, an ideal solution without any interaction is assumed. The coexistence curve in the parameter space of the temperature $T$ and the concentration $C$ of $B$ atoms is then given by

$$C_S(T) = \frac{1 - e^{-\mu_A/T}}{e^{-\mu_B/T} - e^{-\mu_A/T}},$$

$$C_L(T) = \frac{(1 - e^{-\mu_A/T})e^{-\mu_B/T}}{e^{-\mu_B/T} - e^{-\mu_A/T}}. \tag{1}$$

The temperature unit is so chosen that the Boltzmann constant is unity; $k_B = 1$. At a fixed temperature $T$ between the melting temperatures of pure $A$ and $B$ systems, $T_A$ and $T_B$ ($< T_A$), the solution with concentration $C$ smaller than $C_S$ should be in the solid phase, and that with $C$ larger than $C_L$ should be in the liquid. The solution with $C$ between $C_S$ and $C_L$ is in the two-phase region, and the solid and liquid phases are separated by a stationary interface in equilibrium.

At a high temperature in the liquid one-phase region, the solution with concentration $C$ is in a purely random

atomic configuration. On cooling the chain at a fixed concentration $C$ in a solid one-phase or two-phase region, the crystal growth takes place. The diffusionless solidification model in a chain considered by Temkin [1] is the model that the solidification proceeds via the propagation of a single solid-liquid interface along the frozen configuration of $A$ and $B$ atoms. The probability $P(n,t)$ that the chain is solidified up to the $n$th site but is still in the liquid state from the $(n+1)$th site at a time $t$ is assumed to satisfy the master equation

$$\frac{\partial P(n,t)}{\partial t} = \sum_{n'=n\pm1} W(n,n')P(n',t)$$
$$- \sum_{n'=n\pm1} W(n',n)P(n,t). \qquad (2)$$

The transition probability $W(n',n)$ of the interface position from a site $n$ to $n'$ depends on the arrangement of the $AB$ atoms around the interface. When the $n$th site is occupied by an $X$ $(= A$ or $B)$ atom which is solid and the $(n+1)$th site by a $Y$ $(= A$ or $B)$ atom which is liquid, the transition probability for the advancement of the interface is $W(n+1,n) = w_{+Y}$, and that of the retardation is $W(n-1,n) = w_{-X}$. Since the ratio of a particular atom $X$ to be in the liquid and the solid state is given by $e^{-\mu_X/T}$ thermodynamically and by $w_{-X}/w_{+X}$ kinetically, the relation $w_{-X}/w_{+X} = e^{-\mu_X/T}$ should hold.

The theoretical analysis by Temkin [1,2] reveals that the mean displacement of the interface position $\langle n(t) \rangle$ in the solid one-phase region is linear in time as $\langle n(t) \rangle = v_+ t$ with

$$v_+ = (1 - \langle w_-/w_+ \rangle)/\langle 1/w_+ \rangle$$
$$= \left\{ 1 - \left[ C\frac{w_{-B}}{w_{+B}} + (1-C)\frac{w_{-A}}{w_{+A}} \right] \right\} \bigg/ \left[ \frac{1}{w_{+A}} + C\left( \frac{1}{w_{+B}} - \frac{1}{w_{+A}} \right) \right] \qquad (3)$$

and in the liquid one-phase region as $\langle n(t) \rangle = -v_- t$ with

$$v_- = (1 - \langle w_+/w_- \rangle)/\langle 1/w_- \rangle$$
$$= \left\{ 1 - \left[ C\frac{w_{+B}}{w_{-B}} + (1-C)\frac{w_{+A}}{w_{-A}} \right] \right\} \bigg/ \left[ \frac{1}{w_{-A}} + C\left( \frac{1}{w_{-B}} - \frac{1}{w_{-A}} \right) \right]. \qquad (4)$$

At $C_S$ $(C_L)$, the average $\langle w_-/w_+ \rangle$ $(\langle w_+/w_- \rangle)$ is equal to unity and $v_+$ $(v_-)$ vanishes. In the two-phase region, $C_S < C < C_L$, the mean displacement $\langle n(t) \rangle$ is no longer linear in time, and the steady growth velocity vanishes. According to Derrida's general treatment of the one-dimensional hopping model [6], $\langle n(t) \rangle$ shows a power law behavior $\langle n(t) \rangle \sim t^{\nu_1}$ with an exponent $\nu_1$ determined from the relation

$$\left\langle \left( \frac{w_-}{w_+} \right)^{\nu_1} \right\rangle = 1. \qquad (5)$$

He also obtained the expression of the diffusion constant

$$D = \frac{1}{2} \lim_{t \to \infty} \frac{d}{dt} \{ \langle [n(t) - \langle n(t) \rangle]^2 \rangle \}$$
$$= \frac{1 - \left\langle w_-/w_+ \right\rangle^2}{1 - \left\langle (w_-/w_+)^2 \right\rangle} \left\langle \frac{1}{w_+} \right\rangle^{-3} \left[ \left\langle \frac{1}{w_+} \right\rangle \left\langle \frac{w_-}{w_+^2} \right\rangle + \frac{1}{2} \left\langle \frac{1}{w_+^2} \right\rangle \left( 1 - \left\langle \frac{w_-}{w_+} \right\rangle \right) \right], \qquad (6)$$

for the region $\langle (w_-/w_+)^2 \rangle < 1$. When $C$ is larger than

$$C_2 \equiv \frac{1 - (w_{-A}/w_{+A})^2}{(w_{-B}/w_{+B})^2 - (w_{-A}/w_{+A})^2}, \qquad (7)$$

$D$ is expected to diverge even in the one-phase region.

## III. SIMULATION RESULT

In order to understand the fact that the mean displacement and the variance become anomalous at different concentrations, we perform Monte Carlo simulations. When the interface is located betweeen the $X$ solid atom and $Y$ liquid atom, it waits a time $(w_{-X} + w_{+Y})^{-1}$,

and then the interface advances forwards with a probability $w_{+Y}/(w_{-X} + w_{+Y})$ or recedes backwards with a probability $w_{-X}/(w_{-X} + w_{+Y})$. Parameters are chosen as $T_A = 0.9$, $T_B = 0.1$, $L_A/T_A = L_B/T_B = 1$, $T = 0.5$, and thus the equilibrium concentrations are $C_S = 0.310$ and $C_L = 0.690$. At this special temperature $T = 0.5$, the phase diagram is symmetric at the concentration $C = 0.5$. Parameters for the interface dynamics are set as the solidification probabilities being

$w_{+A} = w_{+B} = 1$, and the melting probabilities being $w_{-A} = e^{-0.8} = 0.4493$ and $w_{-B} = e^{0.8} = 2.226$. A chain has a length $L$ of 1000–50 000, and each site is occupied randomly by a $B$ atom with a probability $C$ and by an $A$ atom with a probability $1-C$. The sequence of $AB$ atoms is kept fixed during a whole simulation. The solid-liquid interface is initially set at a site $l_0$ with the solid being
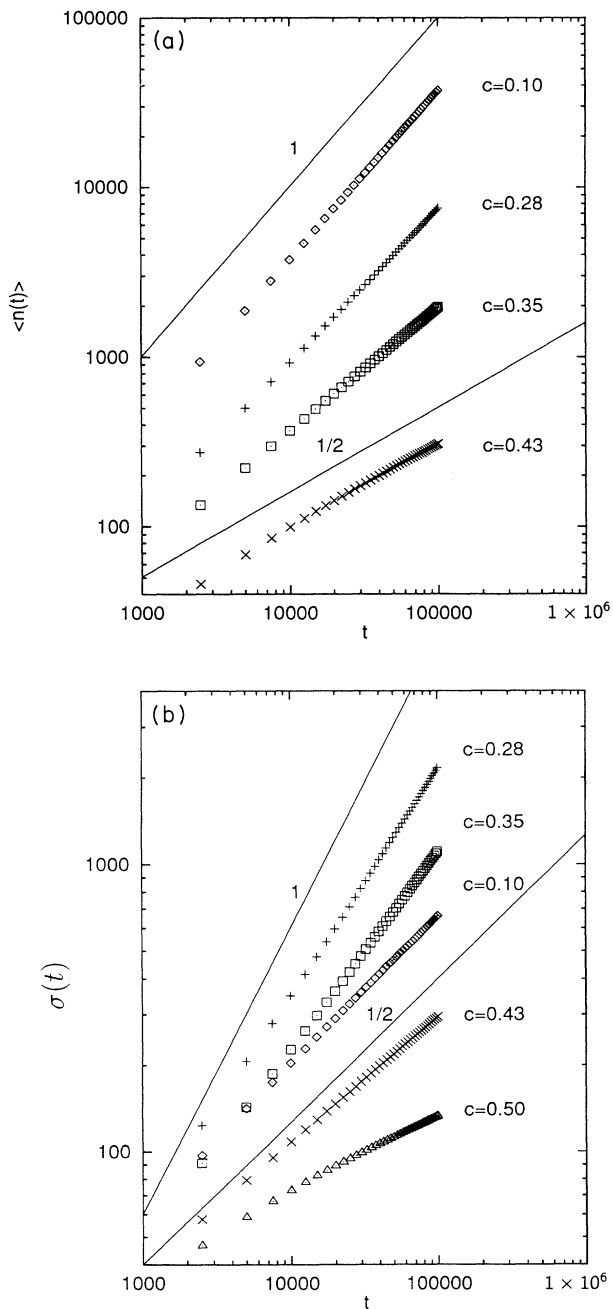


FIG. 1. Time variation of (a) the mean displacement $\langle n(t) \rangle$ and (b) the variance $\sigma(t) = \sqrt{\langle [n(t) - \langle n(t) \rangle]^2 \rangle}$ for various concentrations of $B$ atoms in a both logarithmic way. Two straight lines represent the asymptotic behavior with exponent 1 and 1/2.

in the region $l \leq l_0$ and the liquid being in the region $l > l_0$. The random walk of the interface position has been simulated up to the time $10^5$. Averages of physical quantities have been taken over $10^5$ chains with various $AB$ sequences. The mean displacement $\langle n(t) \rangle \equiv l(t) - l_0 \rangle$ at various concentrations of the $B$ species are plotted in Fig. 1(a). The time dependence is fitted to a single power law of the time as $\langle n(t) \rangle = at^{\nu_1} + b$, and the obtained dynamical exponent $\nu_1$ is plotted in Fig. 2. Up to the equilibrium concentration $C_S = 0.31$, the exponent $\nu_1$ remains about unity, and it starts to decrease on increasing $C$ to the symmetric point $C = 0.5$. By forcing a linear fit of $\langle n(t) \rangle$ to the time $t$, the velocity $v_+$ varies as is shown in Fig. 3, and agrees quite well with the theoretical expectation Eq. (3) in the one-phase region. In the two-phase region, $C_S < C < C_L$, an exponent $\nu_1 = \frac{1}{2}$ is expected by the mean field approximation [3], which is in clear contradiction to the simulation result, since $\nu_1$ depends on the concentration and varies between unity and 0. The variation of $\nu_1$ agrees well with the theoretical expectation (5), which can be simplified in the present case as

$$\nu_1 = 1.25 \ln\left(\frac{1-C}{C}\right), \qquad (8)$$

and is shown by a solid line in Fig. 2. The decrease of the exponent $\nu_1$ in the Bernasconi-Schneider model [4] has been confirmed by a similar Monte Carlo study [10].

The time evolution of the variance $\sigma(t) \equiv \sqrt{\langle [n(t) - \langle n(t) \rangle]^2 \rangle}$ is plotted in Fig. 1(b). It is also fitted to a single power law, $\sigma(t) = a_2 t^{\nu_2} + b_2$, and the exponent $\nu_2$ is shown in Fig. 2. $\nu_2$ starts from $\frac{1}{2}$ of the normal Brownian motion for a pure system, $C = 0$, up to about $C_2 = 0.168$ given by Eq. (7), and increases
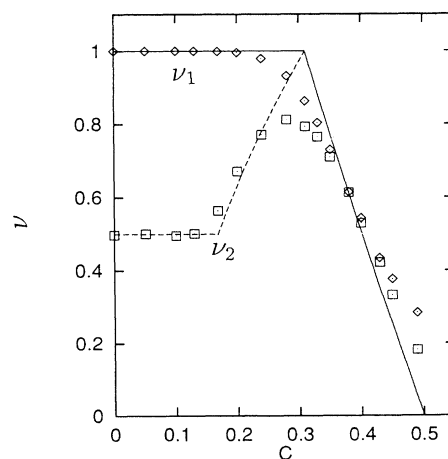


FIG. 2. Exponent $\nu_1$ of the mean displacement, $\langle n(t) \rangle \sim t^{\nu_1}$, and that $\nu_2$ of the variance, $\sigma(t) \sim t^{\nu_2}$, at various concentrations of $B$ atoms. The solid-liquid phase boundary is at $C_S = 0.31$, and the anomaly in $\sigma$ is expected at $C_2 = 0.168$. Solid and dashed lines represent theoretical expectations, Eq. (13), of $\nu_1$ and $\nu_2$, respectively.
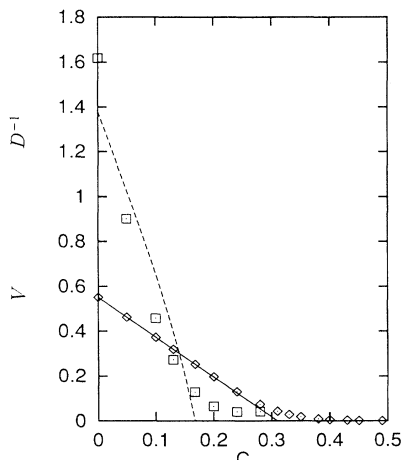
FIG. 3. Linear velocity $v_+$ and the reciprocal diffusion constant $D^{-1}$ versus concentration $C$. Solid and dotted lines represent the theoretical values of $v_+$ [Eq. (3)] and $D^{-1}$[Eq.(6)], respectively.

to 1 near $C_S$. From $C_S$ on, $\nu_2$ decreases similarly with the velocity exponent $\nu_1$. By fitting $\sigma^2(t)$ to the linear growth law for $0 < C < C_2$, the diffusion constant $D$ is obtained and its reciprocal $D^{-1}$ is plotted in Fig. 3. The simulation data agree qualitatively with the theoretical expectation (6), or more appropriately in the present case as

$$D^{-1} = 2\frac{(C_2 - C)}{(C_S - C)}\frac{(e^{0.8} + e^{-0.8})}{[1 + Ce^{0.8} + (1 - C)e^{-0.8}]^2}. \quad (9)$$

Anomalies in the mean displacement and the variance are reflected in the profile of the probability distribution $P(n,t)$. Figure 4 depicts $P(n,t)$ for different concentrations at $C = 0.10$, 0.28, 0.35, 0.43, and 0.5. In the region below $C_2$ the probability $P$ has a steadily moving round peak [Fig. 4(a)] and the profile is almost symmetric about the peak. In the region between $C_2$ and $C_S$ shown in Fig. 4(b), the peak moves steadily but a significant portion of the probability remains at the initial position. This causes the strong broadening and the divergence of diffusion constant $D$. In the region $C_S \leq C \leq 0.40$ shown in Fig. 4(c), the profile of $P$ looks similar to that shown in Fig. 4(b) with the exception that the main peak now shifts slower than linearity in time, and in fact the peak shift has the same time dependence with the width of $P(n,t)$. Deep in the two-phase region at $C \geq 0.40$ as shown in Fig. 4(d), probability $P$ consists solely of a cuspy peak staying stationary at the initial position with an asymmetric long tail. Of course at $C = 0.50$ the peak remains at the origin due to the symmetry, as shown in Fig. 4(e).

Variation of the probability distribution at different times can be summarized into a scaling form. The products of the probability $P$ and the width $\sigma$ at various times are plotted as a function of the normalized position, $(n - \langle n \rangle)/\sigma$, in the one-phase region [Figs. 5(a) and 5(b)], or $n/\sigma$ in the two-phase region [Figs. 5(c)–(e)].
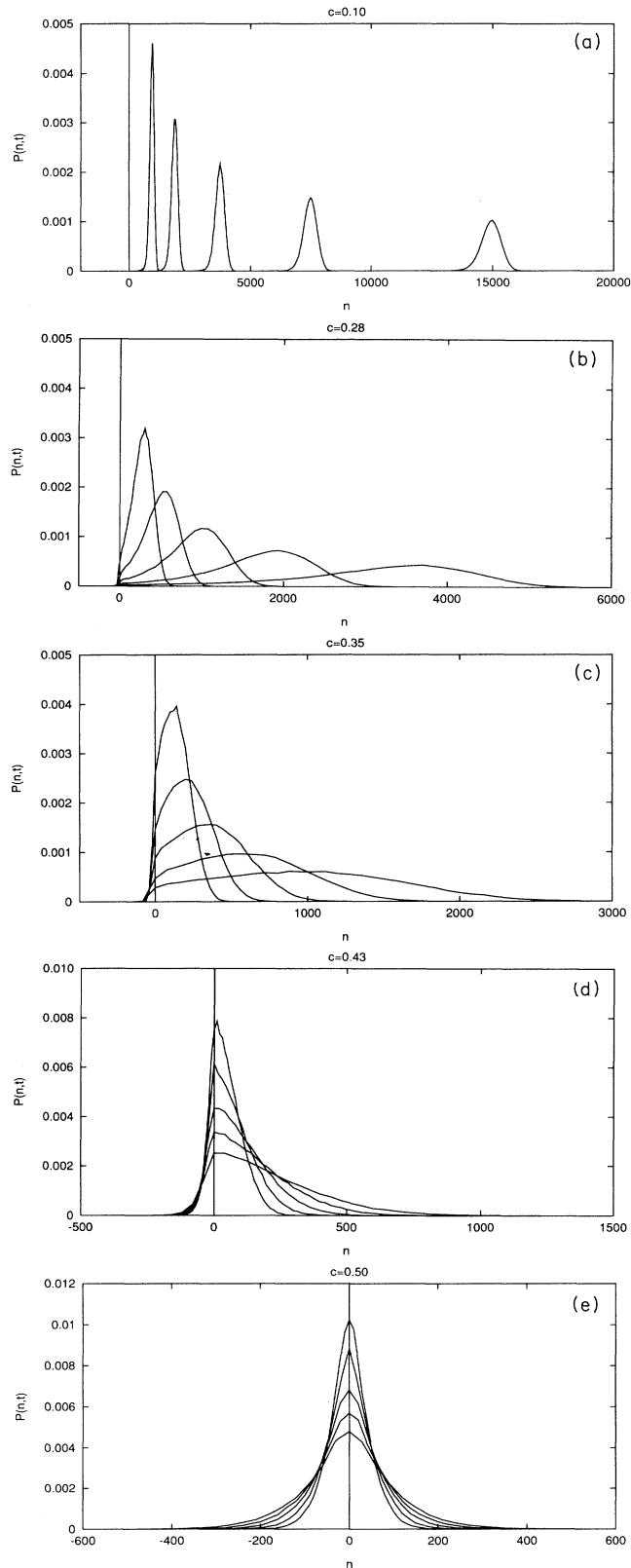


FIG. 4. Probability distribution $P(n,t)$ of finding the interface at position $n$ at time $t \times 10^{-4} = 0.25, 0.5, 1, 2, 4$ with concentrations (a) $C$ =0.10, (b) $C = 0.28$, (c) $C = 0.35$, (d) $C$ =0.43, and (e) $C = 0.50$.

These plots indicate that the probability $P(n,t)$ asymptotically satisfies the scaling relation

$$P(n,t) = \sigma(t)^{-1}\hat{P}(\delta n/\sigma(t)), \qquad (10)$$

with the deviation $\delta n$ from the average position $\langle n(t)\rangle = v_+ t$ in the one-phase region and from the initial position (i.e., origin) in the two-phase region.

## IV. CONCLUSIONS AND DISCUSSIONS

The interface motion between the solid and liquid in a binary chain is studied by Monte Carlo simulations, and the anomalous time dependence of the mean displacement and the variance is obtained. The transition concentrations $C_S$ and $C_2$ and the velocity exponent $\nu_1$ agree well with theoretical calculation [6]. The variance
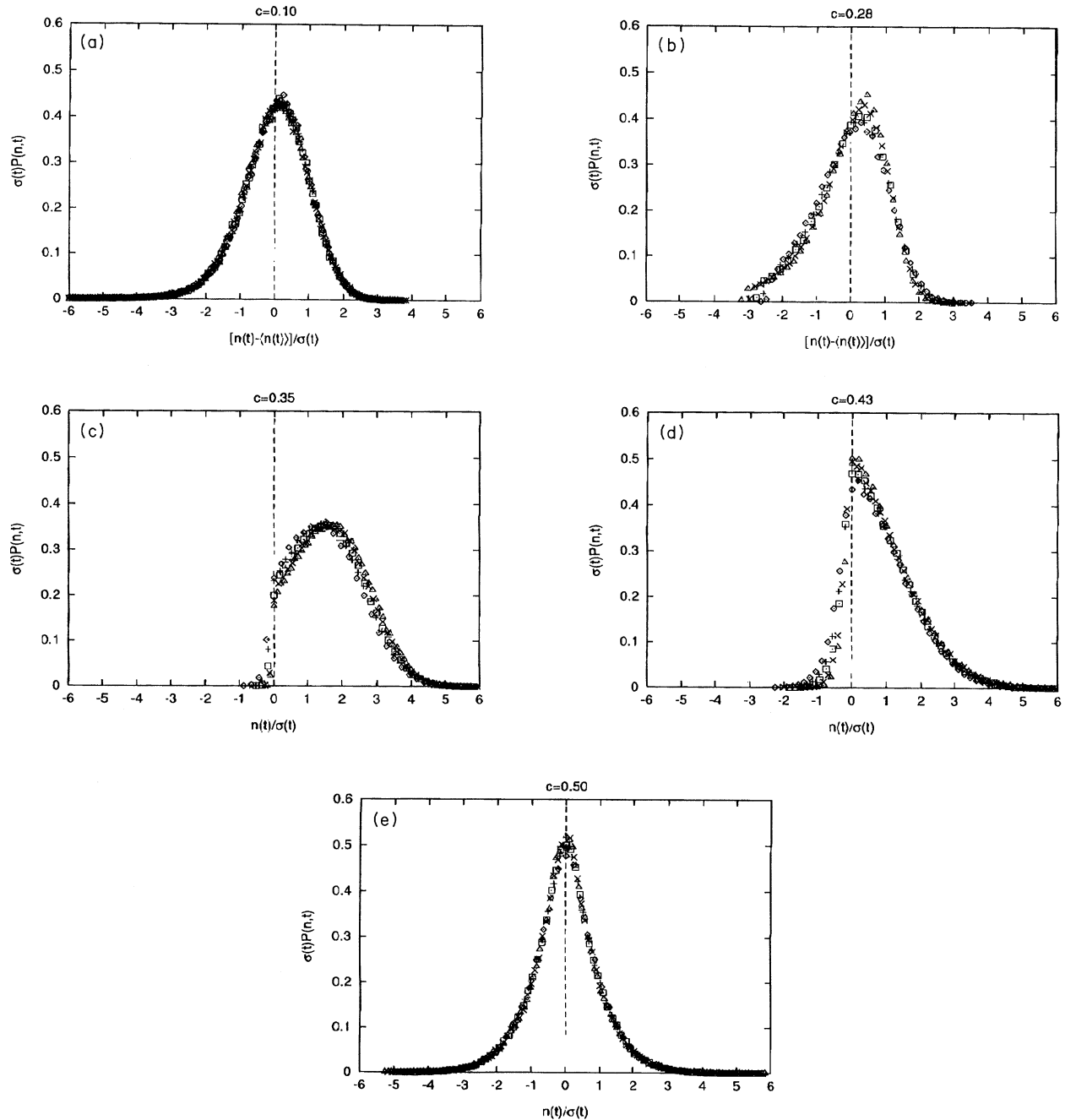


FIG. 5. Scaling plot of the probability $\sigma(t)P(n,t)$ versus $[n - n(t)]/\sigma(t)$ for (a) and (b), or $n/\sigma(t)$ for (c), (d), and (e), for various times $t \times 10^{-4} = 0.25, 0.5, 1, 2, 4$. Concentrations are (a) $C = 0.10$, (b) $C = 0.28$, (c) $C = 0.35$, (d) $C = 0.43$, and (e) $C = 0.50$.

exponent $\nu_2$ shows rather complicated behavior. It remains constant to be $\frac{1}{2}$ for $0 < C < C_2$, increases to unity for $C_2 < C < C_S$, and then decreases to vanish for $C_S < C < 0.5$. Similar complex behavior is found for an exactly soluble model of a directed random walk on a chain [7–9]. In the model, the backward transition rate $W(n - 1, n)$ is set zero and the forward transition rate $W(n + 1, n) = W$ is a random variable with the distribution function $\psi(W)$ in a power law with a cutoff $W_m$ as

$$\psi(W) \sim W^{\mu-1}\hat{\psi}\left(\frac{W}{W_m}\right). \tag{11}$$

Exponents are obtained exactly to be

$$\begin{aligned}
\nu_1 &= \nu_2 = \mu & \text{for} \quad 0 < \mu < 1, \\
\nu_1 &= 1, \ 2\nu_2 = 3 - \mu & \text{for} \quad 1 < \mu < 2, \\
\nu_1 &= 2\nu_2 = 1 & \text{for} \quad 2 < \mu.
\end{aligned} \tag{12}$$

If we replace $\mu$ by $1.25\ln[(1-C)/C]$ following the relation (8), we get the exponents as

$$\begin{aligned}
\nu_1 &= \nu_2 = 1.25\ln[(1 - C)/C] & \text{for} \quad 0.5 > C > C_S, \\
\nu_1 &= 1, \ 2\nu_2 = 3 - 1.25\ln[(1 - C)/C] & \text{for} \quad C_S > C > C_2, \\
\nu_1 &= 2\nu_2 = 1 & \text{for} \quad C_2 > C > 0.
\end{aligned} \tag{13}$$

These results are shown in Fig. 1 and agree fairly well with the simulation result. Therefore, the anomalous time dependence of the diffusionless crystal growth of a binary chain seems to be projected onto that of the random directed walk.

At $C=0.5$, the model reduces to the Sinai model [11]. In this model the variance $\langle n(t)^2 \rangle$ is shown to evolve very slowly as $(\ln t)^4$. This behavior is well observed by plotting $\sqrt{\sigma(t)} = \langle n^2(t) \rangle^{1/4}$ versus $\ln t$, as is shown in Fig. 6.
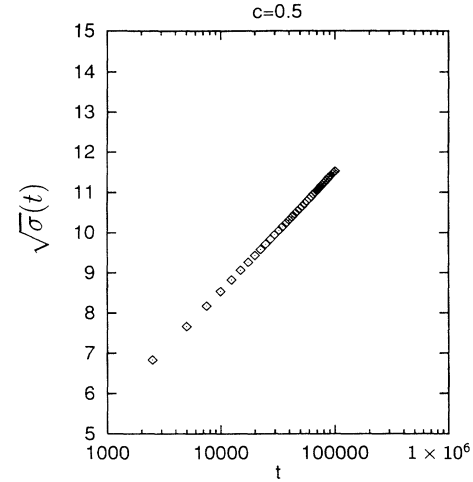


FIG. 6. Semilogarithmic plot of $\sqrt{\sigma(t)}$ versus time $t$ at $C = 0.50$. The result agrees with that of the Sinai model.

[1] D.E. Temkin, J. Cryst. Growth 5, 193 (1969).
[2] D.E. Temkin, Dokl. Akad. Nauk SSSR 206, 27 (1972) [Sov. Math. Dokl. 13, 1172 (1972)].
[3] D.E. Temkin, Kristallografiya 17, 77 (1972) [Sov. Phys. Crystallogr. 17, 60 (1972)].
[4] J. Bernasconi and W.R. Schneider, J. Phys. A 15, L729 (1982).
[5] B. Derrida and Y. Pomeau, Phys. Rev. Lett. 48, 627 (1982).
[6] B. Derrida, J. Stat. Phys. 31, 433 (1983).
[7] C. Aslangul, M. Barthelemy, N. Pottier, and D. Saint-James, J. Stat. Phys. 59, 11 (1990).
[8] J.P. Bouchaud and A. Georges, Phys. Rep. 195, 127 (1990).
[9] J.P. Bouchaud, A. Comtet, A. Georges, and P. Le Doussal, Ann. Phys. 201, 285 (1990).
[10] D.E. Temkin and D. Wolf (unpublished).
[11] Ya. G. Sinai, in Mathematical Problems in Theoretical Physics, edited by R. Schrader, R. Seiler, and P. Uhlenbrock, Lecture Notes in Physics Vol. 153 (Springer, Berlin, 1982), p. 12.