Kinetics of a model for nucleation-controlled polymer crystal growth

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Abstract. The stationary state of a phenomenological model of two-dimensional nucleation-controlled crystal growth is found, using an operator formalism akin to quantum field theory, and the implications for the growth of polymer crystals are briefly discussed. The method also enables a correspondence to be drawn between this problem and that of directed percolation and Reggeon field theory.

1. Introduction

The lamellar morphology is well established in both single polymer crystals grown from solution, and melt-grown crystals whose large-scale structure is spherulitic (Bassett 1981, Keller 1968). The lamellae are characterised by two widely different length scales, two of the edges having dimensions of the order of microns, whilst the third edge, along which the polymer chain axes lie, is typically 100 Å long. Although the observed structure is not a configuration which minimises the free energy, it is apparently the one that forms the fastest, and theories of the growth have been constructed on this basis, assuming that the rate determining step is nucleation of a segment of a crystallising polymer on the growth front (Hoffman *et al* 1976). Such theories aim to calculate the rate of secondary and tertiary nucleation for a lamella of a given size, but a long standing problem has been to relate these to the linear growth rate, purely a problem in statistics. The growth rate is an important experimentally observable quantity, which enables surface energies to be inferred, and additionally provides a sensitive test of these theories (Lauritzen 1973).

In this paper is derived an exact expression for the linear growth rate of a caricature of two-dimensional nucleation-controlled crystal growth hereafter referred to as the Bricklayer Model (BM). The expression for the growth rate interpolates between two physically sensible regimes which are qualitatively different, and whose realisation depends upon the type of crystal being formed. Regime 1 is the case when a given layer of crystal is formed by a single secondary nucleation event, followed by a succession of tertiary nucleation events, whilst regime 2 corresponds to multiple, simultaneous secondary and tertiary nucleation. An important physical effect is that solution-grown crystals are always driven towards regime 2. Although the growth rate was simultaneously and independently derived by Bennett *et al* (1981), the method

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presented here is sufficiently general and systematic that it is of interest in its own right. Furthermore it establishes a connection between the BM, Reggeon field theory and directed percolation, thus showing that the model exhibits a second-order phase transition.

The solution of the BM relies on a correspondence between the interface of the two-dimensional crystal and a one-dimensional gas of particles (kinks) and anti-particles (antikinks) which may be created or annihilated in pairs. A statistical description of such a system must include not only the time evolution of N-particle states, but also transitions between states of different particle number. Thus an ensemble of distribution functions needs to be considered, which leads to a Fock space description of the system, and the formal device of introducing annihilation and creation operators. Field theoretic methods have been used previously to describe other classical systems without particle number conservation, namely chemical reactions (Doi 1976, Grassberger and de la Torre 1979), and cross-linked rubbers (Edwards and Freed 1970).

The organisation of this paper is as follows. In § 2, the BM is described and some elementary arguments given for the behaviour. In § 3 the second quantisation formalism is presented; this differs in several important respects from the conventional formulation in quantum field theory. Section 4 formulates the BM using the formalism of the previous section and hence presents the exact solution. It is also shown how to derive the BBGKY equations for the kink distribution functions. Finally, in § 5, it is shown that a generalisation of the BM is equivalent to the statistics of directed lattice animals (Redner 1982) and Reggeon Field Theory (RFT) (Moshe 1978).
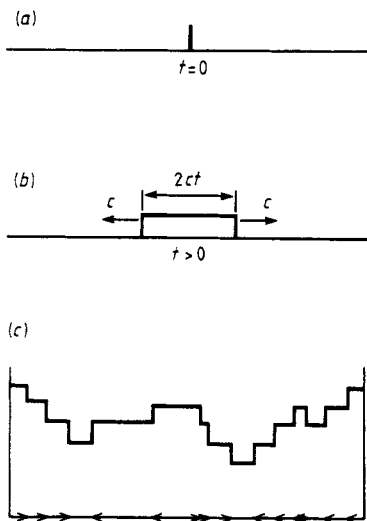
2. The bricklayer model

Polymer crystals may be formed by supercooling a polymer solution or a polymer melt, and the resulting morphology is quite different in these two cases. From a solution polymer single crystals are obtained whose lamellar appearance is sketched in figure 1(a). Crystallisation from the melt results in a large-scale spherulitic structure, composed of thin ribbon-like lamellae radiating out from the centre of the spherulite, as shown in figures 1(b, c). Thus, we idealise the polymer crystal as a two-dimensional object, which grows by the nucleation and lateral growth along the interface of 'bricks' from the liquid (Sanchez and DiMarzio 1971). The bricks are, in reality, segments of polymer coils, which lie parallel to the short edge when they are incorporated into the crystal, and thus are connected in some manner by folds. We will largely ignore the
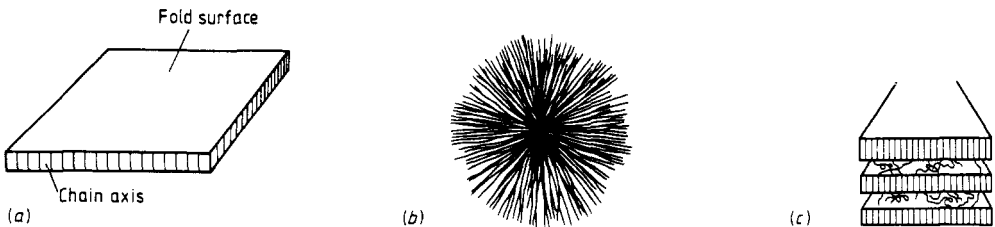
Figure 1. (a) Polymer single crystal lamella. (b) Spherulite consisting of chain folded lamellae radiating from a central point. (c) Magnified end-on view of spherulite, showing stacks of lamellae and interlamellar links. The radial distance R is so large that L is virtually independent of R.

connectivity in the following discussion, on the grounds that this is a microscopic effect which will be included in the rate of nucleation per unit length, μ, and in the lateral spreading speed c. We will, however, assume that the connectivity constraint requires that a deposited brick remains in the crystal and is not re-dissolved.

The formation of a nucleus consisting of a single brick on an otherwise flat interface creates two adjacent sites where subsequent deposition is most favoured. These are energetically advantageous by virtue of the fact that deposition of a brick in these sites does not create as many new surfaces as a new nucleation event. The evolution of the system starting from a flat interface is illustrated in figure 2.

Figure 2. Dynamics of the bricklayer model. In (a), a nucleation event occurs on a flat interface, and spreads laterally (b) with speed c. A typical section of a growth front profile at a much later time, with multiple nucleation, is shown in (c). The position of the kinks and antikinks is shown.

The most important point about the dynamics we have specified is that the resulting interface has no overhangs, allowing us to make a trivial but nevertheless crucial observation which is the basis of all that follows. We consider figure 1(c) and imagine that the position of the right-moving edges (kinks) and the left-moving edges (antikinks) are projected onto a line, the x axis. For convenience, we distinguish between them by an arrow ($>$ or $<$) indicating the direction of motion. If the height of the growth front above some origin is $h(x)$, and the microscopic densities of the kinks and antikinks are respectively

$$\rho_>(x) = \sum_i \delta(x - x_>(i)) \tag{2.1a}$$

$$\rho_<(x) = \sum_j \delta(x - x_<(j)) \tag{2.1b}$$

then

$$\mathrm{d}h/\mathrm{d}x = \rho_<(x) - \rho_>(x). \tag{2.2}$$

There is a slight ambiguity in that a genuine double step on the crystal cannot be represented by this scheme. Such a case can only have arisen by two simultaneous nucleations at the same point, an event which is of measure zero in our continuum model, although two arbitrarily close nucleations may, of course, be represented.

The dynamics of the kinks/antikinks on the line is very simple. They are particles moving in one dimension at a constant velocity $\pm c$, which may be created anywhere on the substrate with probability μ per unit length per unit time, and which have the property that kinks and antikinks are genuine antiparticles. They are created in pairs and annihilate in pairs when they collide. The detailed behaviour of such a system is given in § 4.

Before giving some heuristic arguments for the behaviour of the BM, it is convenient to discuss the boundary conditions, since there are three distinct types which can occur, corresponding to different substrate topologies. Firstly, the substrate may have the topology of a line segment of length L, in which case we require that

$$\rho_>(-\tfrac{1}{2}L) = \rho_<(\tfrac{1}{2}L) = 0 \tag{2.3}$$

since kinks (antikinks) cannot be created in $x < -\tfrac{1}{2}L(x > \tfrac{1}{2}L)$. This is an appropriate description of melt-grown crystals, where L is the length of the outward-facing growth front presented to the melt. The other boundary conditions which we wish to consider are periodic boundary conditions where the crystal either grows in a plane, so that the substrate length changes with time, or where the crystal grows vertically above the substrate, whose length remains fixed. The former corresponds to solution-grown single crystals which are tabular, whilst the latter may be realised in certain biological structures such as microtubules, flagella, and cilia. These distinctions between the boundary conditions have important consequences for the growth of polymer crystals, which may be understood from the elementary considerations given below.

We may distinguish three regimes of growth behaviour. The simplest case (regime 1) is when the lateral growth rate c is sufficiently fast that the progeny of a single nucleation event cover the substrate before the next nucleation event occurs, namely

$$1/\mu L \gg L/c. \tag{2.4}$$

The linear growth rate in this regime is just

$$G = b\mu L \tag{2.5}$$

where b is the height of a brick. When (2.4) is not satisfied, multiple nucleation is occurring, as depicted in figure 1(c); in order to make progress, we may assume that the system with periodic boundary conditions is in a steady state with $2N$ kinks and antikinks uniformly distributed over the substrate. Equating the rate of creation with the rate of annihilation yields the regime 2 results

$$N = (\mu/2c)^{1/2}L \tag{2.6}$$

and

$$G = b(2\mu c)^{1/2}. \tag{2.7}$$

Regime 3 occurs when the nucleation rate is sufficiently great that it is no longer adequate to treat the substrate as consisting of a continuum of sites. If the mean free path of a kink/antikink is of the order of a stem width then we must use a discrete model of uncorrelated nucleation events i.e. a Poisson process for which the growth rate is once again proportional to μ.

The important point to notice is that in (2.5) the growth rate G is proportional to L, whilst in (2.7) G is independent of L. For a solution-grown crystal

$$G \propto dL/dt \tag{2.8}$$

and so if the growth conditions of regime 1 pertain, the crystal will grow exponentially until (2.4) is violated. Thereafter the growth kinetics are those of regime 2, and the growth rate is independent of time. This is not the case for melt-grown crystals, where the growth front has the topology of a line, and the substrate length is practically independent of the radius of the spherulite. Thus melt-grown crystals may be observed in either regime whereas solution-grown crystals in the late stages of growth will be in either regime 2, or in a regime intermediate between regime 1 and regime 2. The calculation in § 4 which forms the main body of this paper derives the details of the cross-over between regime 1 and regime 2.

3. Second quantisation formalism for classical statistical systems

Consider a classical system with no degrees of freedom other than the particle number. We suppose that the state Ψ of the system can be described by the probability of finding n particles at time t, $P(n, t; \Psi)$, and that the state Ψ is a vector in a linear Hilbert space so that

$$P(n, t; a\Psi_1 + b\Psi_2) = aP(n, t; \Psi_1) + bP(n, t; \Psi_2) \tag{3.1}$$

where a and b are complex numbers. We shall find it more convenient to discuss the generating function

$$\Gamma(s, t; \Psi) = \sum_n s^n P(n, t; \Psi) \tag{3.2}$$

normalised so that

$$\Gamma(0, t; \Psi) = 1. \tag{3.3}$$

This is related to the moments of the distribution P by

$$\Gamma_k(\Psi) \equiv \langle n(n-1)(n-2) \ldots (n-k+1)\rangle = \partial^k \Gamma / \partial s^k |_{s=1}. \tag{3.4}$$

To complete the description of the Hilbert space, we must define an inner product, and several possibilities present themselves, which we shall distinguish by the typeface of the brackets. If we are mainly interested in discussing Γ then it is most convenient to use

$$\{\Psi_1 | \Psi_2\} = \sum_k \frac{1}{k!} \Gamma_k^*(\Psi_1) \Gamma_k(\Psi_2) \tag{3.5}$$

but we shall have occasion to use

$$\langle \Psi_1 | \Psi_2 \rangle = \sum_n n! P^*(n; \Psi_1) P(n; \Psi_2). \tag{3.6}$$

Since we are interested in the particle number, a convenient orthogonal basis set is provided by the n-particle states $|n\rangle$, satisfying

$$\langle m | n \rangle = n! \delta_{mn}, \tag{3.7}$$

in terms of which

$$P(n; \Psi) = (1/n!)\langle n|\Psi\rangle. \tag{3.8}$$

Denoting operators by a caret, we introduce the annihilation and creation operators $\hat{a}$ and $\hat{c}$ respectively, defined by

$$\hat{c}|n\rangle = |n+1\rangle, \qquad \hat{a}|n\rangle = n|n-1\rangle \tag{3.9a, b}$$

which satisfy

$$\hat{a}\hat{c} - \hat{c}\hat{a} \equiv [\hat{a}, \hat{c}] = 1. \tag{3.10}$$

As usual, these act on the bras dual to the kets $|n\rangle$ to give

$$\langle m|\hat{a} = \langle m+1|, \qquad \langle m|\hat{c} = \langle m-1|m \tag{3.11a, b}$$

showing that $\hat{a}$ and $\hat{c}$ are adjoints (denoted by $\hat{a}^+ = \hat{c}$) with respect to (3.6). The vacuum state is given by

$$\hat{a}|0\rangle = \langle 0|\hat{c} = 0. \tag{3.12}$$

With these rules it is easy to prove the closure relation

$$\sum_n |n\rangle \frac{1}{n!} \langle n| = \sum_n \hat{c}^n|0\rangle \frac{1}{n!} \langle 0|\hat{a}^n = 1 \tag{3.13}$$

and to show that the representations of the probability distribution, the generating function and the moments are given by

$$P(n; \Psi) = (1/n!)\langle 0|\hat{a}^n|\Psi\rangle \tag{3.14}$$

$$\Gamma(s; \Psi) = \langle 0|e^{\hat{a}s}|\Psi\rangle \tag{3.15}$$

$$\Gamma_k(\Psi) = \langle 0|\hat{a}^k e^{\hat{a}}|\Psi\rangle. \tag{3.16}$$

The relation between (3.5) and (3.6) is then

$$\{\Psi_1|\Psi_2\} = \langle \Psi_1|e^{\hat{c}}e^{\hat{a}}|\Psi_2\rangle \tag{3.17}$$

and the matrix elements of some arbitrary operator $\hat{A}$ are given by

$$\{\Psi_1|\hat{A}|\Psi_2\} = \langle \Psi_1|e^{\hat{c}} e^{\hat{a}}\hat{A}|\Psi_2\rangle. \tag{3.18}$$

It is easy to show that the adjoint with respect to (3.5), denoted by ‡, is

$$\hat{a}^\ddagger = \hat{c} - 1. \tag{3.19}$$

In this representation we find

$$P(n; \Psi) = (1/n!)\{0|e^{-\hat{a}}\hat{a}^n|\Psi\} \tag{3.20}$$

$$\Gamma(s; \Psi) = \{0|e^{\hat{a}(s-1)}|\Psi\} \tag{3.21}$$

$$\Gamma_k(\Psi) = (1/k!)\{0|\hat{a}^k|\Psi\} \tag{3.22}$$

where the normalisation condition is

$$\{0|\Psi\} = 1. \tag{3.23}$$

We complete the discussion of this simple system by describing the time evolution of Markov processes. We define the operator $\hat{L}$ which is just the Liouvillian when the

dynamics is deterministic (and we shall retain this name even for stochastic dynamical systems), by the time evolution equation

$$(d/dt)|\Psi(t)\rangle = \hat{L}|\Psi(t)\rangle. \tag{3.24}$$

The only requirement on $\hat{L}$ is that it conserves probability, so that

$$\{0|\hat{L} = 0. \tag{3.25}$$

Unlike the Hamiltonian in quantum mechanics, $\hat{L}$ is not necessarily Hermitian. To illustrate how to construct $\hat{L}$, we consider the chemical reaction

$$nX \rightarrow n'X \tag{3.26}$$

where k is the rate constant. For this reaction, one might expect the Liouvillian to be

$$\hat{L} = k\hat{c}^{n'}\hat{a}^n. \tag{3.27}$$

This, however, does not conserve probability, and we need to subtract a term with $\hat{a}^n$ to the right of any creation operators. The number of creation operators is determined by the requirement that the new term must not change the particle number. These considerations lead to

$$\hat{L} = k(\hat{c}^{n'} - \hat{c}^n)\hat{a}^n \tag{3.28}$$

which does indeed satisfy (3.23). The additional term in the Liouvillian represents the probability that the system does not make a transition in the time interval dt. Apart from this subtlety, the determination of the Liouvillian is quite straightforward. Usually we are interested in the time development of the probability distribution, which is easily obtained from

$$dP(m; \Psi)/dt = (1/m!)\langle 0|\hat{a}^m\hat{L}|\Psi\rangle. \tag{3.29}$$

By commuting $\hat{L}$ past $\hat{a}^m$ we derive the master equation

$$dP(m, t)/dt = \sum_{m'} \{W(m, m')P(m', t) - W(m', m)P(m, t)\} \tag{3.30}$$

with the transition probabilities $W(m, m')$ given by

$$W(m, m') = k\delta^{(K)}(m' + n' - m - n)\binom{m'}{n} n! \tag{3.31}$$

where $\delta^{(K)}$ is the Kronecker delta function.

The formalism outlined above can be extended in many ways; in particular, systems with a finite or an infinite number of degrees of freedom can be described and a renormalised perturbation theory developed. These refinements are not needed here; it suffices to state the generalisation for a system with an extra degree of freedom, namely the position, x, of the particles along a line.

We define creation and annihilation operators respectively by

$$\hat{\sigma}(x)|x_1, x_2, x_3, \ldots, x_n\rangle = |x_1, x_2, x_3, \ldots, x_n, x\rangle \tag{3.32}$$

$$\hat{\psi}(x)|x_1, x_2, x_3, \ldots, x_n\rangle = \sum_{i=1}^{n} \delta(x - x_i)|x_1, x_2, \ldots, x_{i-1}, x_{i+1}, \ldots, x_n\rangle \tag{3.33}$$

where $\delta(x)$ is the Dirac delta function. Thus the commutation rule

$$[\hat{\psi}(x), \hat{\sigma}(y)] = \delta(x - y) \tag{3.34}$$

is satisfied, and the adjoints in the two representations are given by

$$\hat{\sigma}(x) = \hat{\psi}^{\dagger}(x) = \hat{\psi}^{\ddagger}(x) + 1. \tag{3.35}$$

The natural generalisations of P and Γ_k are the distribution function $f_n(x_1 \ldots x_n; \Psi)$ and the k-particle distribution function $\rho_k(x_1 \ldots x_k; \Psi)$, which are respectively the probability that there are exactly n particles in the system at $x_1, x_2, \ldots, x_n$, and the probability that k particles can be found in the positions $x_1 \ldots x_k$. These are related to P and Γ_k by

$$P(n; \psi) = \frac{1}{n!} \int \prod_{i=1}^{n} \mathrm{d}x_i f_n(\{x_i\}; \Psi) \tag{3.36}$$

$$\Gamma_k = \int \prod_{i=1}^{k} \mathrm{d}x_i \rho_k(\{x_i\}; \Psi) \tag{3.37}$$

with

$$f_n(x_1, \ldots, x_n; \Psi) = \langle 0|\hat{\psi}(x_1) \ldots \hat{\psi}(x_n)|\Psi\rangle$$
$$= \{0|\hat{\psi}(x_1) \ldots \hat{\psi}(x_n) e^{-\int \mathrm{d}x \, \hat{\psi}(x)}|\Psi\} \tag{3.38}$$

$$\rho_k(x_1 \ldots x_k; \Psi) = \langle 0|e^{\int \mathrm{d}x \, \hat{\psi}(x)} \hat{\psi}(x_1) \ldots \hat{\psi}(x_k)|\Psi\rangle$$
$$= \{0|\hat{\psi}(x_1) \ldots \hat{\psi}(x_k)|\Psi\}. \tag{3.39}$$

Here the generalisation of the inner products (3.5) and (3.6) are

$$\{\Psi_1|\Psi_2\} = \sum_k \frac{1}{k!} \int \prod_{i=1}^{k} \mathrm{d}x_i \rho_k^*(x_1 \ldots x_k; \Psi_1) \rho_k(x_1 \ldots x_k; \Psi_2) \tag{3.40}$$

and

$$\langle \Psi_1|\Psi_2 \rangle = \sum_n n! \int \prod_{i=1}^{n} \mathrm{d}x_i f_n^*(x_1 \ldots x_n; \Psi_1) f_n(x_1 \ldots x_n; \Psi_2). \tag{3.41}$$

We conclude this section by briefly comparing and contrasting the present formalism with the second quantisation formalism in quantum mechanics. Firstly, probability in quantum mechanics is proportional to the modulus squared of some matrix element, whereas here the matrix elements are directly related to the probability. Secondly, the Liouvillian is not necessarily Hermitian since the norm of a state vector is not necessarily constant as a function of time. Thirdly, as a consequence of the probability being proportional to the matrix elements, there is no equivalent of the antisymmetric wavefunction of fermions. When we do have occasion in § 5 to introduce fermion-like objects, their algebra will be slightly different from quantum mechanical fermions.

4. Stationary solution of the bricklayer model

Consider a substrate of length M with periodic boundary conditions. We describe the kinks and antikinks by two sets of annihilation and creation operators, labelled by $>$ or $<$ to indicate the particle type. Operators for different particle species commute.

We find the stationary solution of the BM by using the field theoretic formalism to construct the Liouvillian for the model, and thus to derive the differential equation for the generating function, which is exactly soluble.

The Liouvillian consists of combinations of operators to describe the following dynamics:

(1) Kink–antikink, creation at a rate μ per unit length.

(2) Kink–antikink annihilation. In a time interval δt, kink–antikink pairs will annihilate if they are within a distance $2c\delta t$, provided that there are no intervening particles.

(3) Propagation at a velocity $\pm c$.

The creation term is found by analogy with the chemical reaction considered in the preceding section. It is just

$$\hat{L}_{(1)} = \int_0^M \mu[\hat{\sigma}_<(x)\hat{\sigma}_>(x) - 1]\,\mathrm{d}x \tag{4.1}$$

where the term -1 conserves probability. The annihilation term is most easily derived by recalling that the Liouvillian is the generator of infinitesimal displacements in time, so that in the time interval δt

$$\hat{L}_{(2)}\delta t = \int_0^M 2c\delta t[\hat{\psi}_>(x)\hat{\psi}_<(x) - \hat{\sigma}_>(x)\hat{\psi}_>(x)\hat{\sigma}_<(x)\hat{\psi}_<(x)](1 - \hat{v})\,\mathrm{d}x \tag{4.2}$$

where $\hat{v}$ represents the probability that there are no intervening particles between pairs of antiparticles with $2c\delta t$ of each other, and is given by

$$\hat{v} = \int_{x-c\delta t}^{x+c\delta t} \hat{\sigma}_>(x')\hat{\psi}_>(x')\hat{\sigma}_<(x')\hat{\psi}_<(x')\,\mathrm{d}x'. \tag{4.3}$$

In the limit $\delta t \to 0$ this term vanishes, leaving

$$\hat{L}_{(2)} = 2c \int_0^M [\hat{\psi}_>(x)\hat{\psi}_<(x) - \hat{\sigma}_>(x)\hat{\psi}_>(x)\hat{\sigma}_<(x)\hat{\psi}_<(x)]\,\mathrm{d}x. \tag{4.4}$$

The propagation term is obtained by considering a short time interval δt in which a kink moves a distance $c\delta t$, so that it is effectively destroyed at x and created at $x + c\delta t$, i.e.

$$\hat{L}_{(3)}\delta t = \int_0^M [\hat{\psi}^+(x + c\delta t) - \hat{\psi}^+(x)]\hat{\psi}(x). \tag{4.5}$$

Integrating by parts and using periodic boundary conditions leaves

$$\hat{L}_{(3)} = -c \int_0^M \mathrm{d}x\, \hat{\psi}^+(x) \frac{\mathrm{d}\hat{\psi}(x)}{\mathrm{d}x}. \tag{4.6}$$

The normal ordered Liouvillian $\hat{L}$ is then

$$\hat{L} = \hat{L}_{(1)} + \hat{L}_{(2)} + \hat{L}_{(3)}. \tag{4.7}$$

An immediate consequence is that the difference in the number of kinks and antikinks, Δn is a constant of the motion. This physically obvious feature arises because

$$\Delta\hat{n} = \int_0^M \mathrm{d}x[\hat{\psi}_>^+(x)\hat{\psi}_>(x) - \hat{\psi}_<^+(x)\hat{\psi}_<(x)] \tag{4.8}$$

commutes with the Liouvillian so that

$$(d/dt)\{0|\Delta\hat{n}|\Psi\} = 0. \tag{4.9}$$

Let us assume that initially there were neither kinks nor antikinks, and discuss the generating function Γ, whose equation of motion is

$$\frac{d\Gamma}{dt} = \sum_{n=0}^{\infty} \frac{s^n}{(n!)^2} \int_0^M dx_1 \dots dx_n \, dx_1' \dots dx_n' \langle 0|\hat{\psi}_>(x_1) \dots \hat{\psi}_>(x_n)\hat{\psi}_<(x_1') \dots \hat{\psi}_<(x_n')\hat{L}|\Psi\rangle. \tag{4.10}$$

We are interested in the stationary solution for Γ, which, by symmetry, is a uniform kink/antikink distribution. As before, the procedure is to commute $\hat{L}$ past the field operators, using the result that

$$\langle 0|\hat{\psi}(x_1) \dots \hat{\psi}(x_n)\hat{\psi}^+(x) = \langle 0| \sum_{j=1}^{n} \left(\prod_{k\neq j} \hat{\psi}(x_k) \right) \delta(x - x_j). \tag{4.11}$$

$\hat{L}_{(1)}$ contributes $\mu M(s-1)\Gamma(s, t)$. Using the symmetry relation

$$\int_0^M dx \, \hat{\psi}_>(x)\hat{\psi}_<(x)|\Psi\rangle = \frac{1}{M} \int_0^M \int_0^M dx \, dy \, \hat{\psi}_>(x)\hat{\psi}_<(y)|\Psi\rangle \tag{4.12}$$

valid for a state $|\Psi\rangle$ describing a uniform distribution we find that $\hat{L}_{(2)}$ contributes

$$\frac{2c}{M} \left[\frac{d}{ds} \left(s\frac{d}{ds} \right) - \left(s\frac{d}{ds} \right)\left(s\frac{d}{ds} \right) \right] \Gamma(s, t).$$

$\hat{L}_{(3)}$ makes no contribution since it does not change the particle number. Thus, in the steady state Γ satisfies

$$\left(\frac{d^2}{dy^2} + \frac{1}{y} \frac{d}{dy} - 1 \right) \Gamma(y) = 0 \tag{4.13}$$

where we have introduced the dimensionless parameter

$$z = (2\mu/c)^{1/2}M \tag{4.14}$$

and made the change of variables

$$s = (1/z^2)y^2. \tag{4.15}$$

The normalised solution of (4.13) which is regular at the origin is

$$\Gamma(s) = I_0(s^{1/2}z)/I_0(z) \tag{4.16}$$

where I_0 is the modified Bessel function of zeroth order. The growth rate is simply

$$G = (2bc/M)\langle n \rangle \tag{4.17}$$

which reduces to

$$G = b(2\mu c)^{1/2}I_1(z)/I_0(z) \tag{4.18}$$

where $I_1(z) = dI_0/dz$. This result has also been obtained independently by Bennett *et al* (1981). The function I_1/I_0 possesses the limits

$$\frac{I_1(z)}{I_0(z)} = \begin{cases} 1 - 1/2z + O(1/z^2) & z \gg 1 \\ \frac{1}{2}z(1 - z^2/8 + O(z^4)) & z \ll 1 \end{cases} \tag{4.19}$$

and so (2.5) and (2.7) are recovered in their respective limits.

Finally, we derive the BBGKY equations for the system. We consider the quantities

$$\rho^{(k,s)}(x_1 \ldots x_k; x_1' \ldots x_s'; \Psi) = \{0|\hat{\psi}_>(x_1) \ldots \hat{\psi}_>(x_k)\hat{\psi}_<(x_1') \ldots \hat{\psi}_<(x_s')|\Psi\} \quad (4.20)$$

which are the natural extensions of (3.39) for a system with two types of particle. The equation of motion for $\rho^{(k,s)}$ is obtained by replacing $|\Psi\}$ by $\hat{L}|\Psi\}$ in (4.20) and commuting $\hat{L}$ past the field operators, a convenient way being to replace $\hat{\psi}^+$ by $\hat{\sigma}$ in $\hat{L}$ and to use

$$\{0|\hat{\sigma} = \{0|. \quad (4.21)$$

The equation of motion for the (e.g.) kink one-particle distribution functions

$$\langle n_>(x, t)\rangle = \{0|\hat{\psi}_>(x)|\Psi(t)\} \quad (4.22)$$

is obtained by adding the following contributions. The nucleation term gives

$$\mu \int_0^M dy\{0|\hat{\psi}_>(x)\hat{\sigma}_>(y) - \hat{\psi}_>(x)|\Psi\} = \mu. \quad (4.23)$$

The recombination term gives

$$2c \int_0^L dy\{0|\hat{\psi}_>(x)[\hat{\psi}_<(y)\hat{\psi}_>(y) - \hat{\sigma}_>(y)\hat{\psi}_<(y)\hat{\psi}_>(y)]|\Psi\} = 2c\{0|\hat{\psi}_>(x)\hat{\psi}_<(x)|\Psi\}. \quad (4.24)$$

The propagation term gives

$$-c \int_0^M dy\left\{0\left|\hat{\psi}_>(x)\hat{\sigma}_>(y)\frac{d\hat{\psi}_>(y)}{dy}\right|\Psi\right\} = -c\left\{0\left|\frac{d\hat{\psi}_>}{dx}\right|\Psi\right\}. \quad (4.25)$$

In conclusion, we find the coupled equations

$$(\partial/\partial t + c\,\partial/\partial x)\langle n_>(x, t)\rangle = \mu - 2c\langle n_>(x, t)n_<(x, t)\rangle \quad (4.26a)$$

$$(\partial/\partial t - c\,\partial/\partial x)\langle n_<(x, t)\rangle = \mu - 2c\langle n_>(x, t)n_<(x, t)\rangle \quad (4.26b)$$

where, as usual, the one-particle distribution function involve the two-particle distribution function. If we make the mean-field approximation

$$\langle n_>(x, t)n_<(x, t)\rangle = \langle n_>(x, t)\rangle\langle n_<(x, t)\rangle \quad (4.27)$$

which neglects correlations, equations (4.26) become identical to that of Frank (1974).

5. Generalised bricklayer model

In this last section we briefly examine the consequences of allowing the bricks to evaporate at a rate k once they been deposited on the surface. In this generalised bricklayer model (GBM) there is a competition between the tendency for bricks to evaporate and their covering the substrate. In the limit of $k = 0$, namely the BM, a single nucleation event is sufficient to cover the substrate. As k increases from zero there comes a point k_c beyond which the crystal will no longer grow in the substrate. I shall argue that this is a second-order phase transition, by showing that the deposition of the first layer on an existing smooth substrate is related to the problems of directed percolation (DP) and Reggeon field theory (RFT), which have been shown to be equivalent (Cardy and Sugar 1980).

A picturesque way of seeing this is to consider the world lines of the kinks and antikinks, as shown in figure 3. Figure 3(a) shows the world lines for the BM. Points A and D represent nucleation events, whilst B and C represent annihilations. The trajectory labelled 1(2) is the history of the first (second) layer and so on. In figures 3(b, c) are depicted the world lines with $k \neq 0$, where, for simplicity, only one nucleation event is shown. Figure 3(b) is the case when $k > k_c$ and the ultimate fate of the kink–antikink pair is recombination. Point A represents nucleation, whilst B and C are evaporations, and D is the eventual recombination. In figure 3(c), $k < k_c$, and
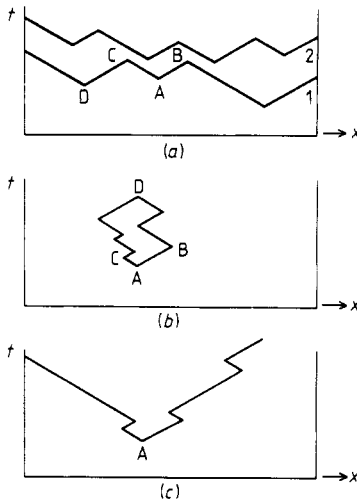
Figure 3. World lines of kinks. (a) Bricklayer model. (b) Generalised bricklayer model, $k > k_c$. (c) Generalised bricklayer model, $k < k_c$.

there is no recombination. Of course, k_c may not exist, but the crux of the argument is that the graphs generated by the GBM are precisely those of directed percolation for which it is known that k_c exists, and is a second-order phase transition. To be precise, we consider a two-dimensional square lattice, with diodes oriented with respect to the axis $n = (1, 1)$, as in figure 4. Each pair of nearest-neighbour sites may be joined by a directed bond or diode pointing 'north-east' or 'north-west', with probability p. A cluster or lattice animal is defined as a structure of connected lattice sites, which in the case of directed percolation must have an origin, marked A in figure 4(a). The clusters are characterised by two correlation lengths, one parallel and one perpendicular to n, as shown in figure 4(b) which diverge as $p \to p_c$, the percolation threshold. The former diverges faster than the latter as $p \to p_c^-$. At $p = p_c$ long-range connectedness sets in only along the n axis, and as p increases, percolation occurs in an ever-widening cone whose limiting semi-angle is $\pi/2$ (Redner and Coniglio 1982, Day and Lubensky 1982). The concentration of the lattice animals and the probability p are related to the parameters in the GBM, but not in a simple way.

This heuristic argument can be made quantitative by showing that the GBM can be mapped into RFT, which is equivalent to DP (Cardy and Sugar 1980). We consider the substrate as a one-dimensional lattice of sites, each of which may be occupied by at most one particle. As before, we shall employ a field theoretic description, but this time we shall use fermion-type operators acting on kets giving the occupation number
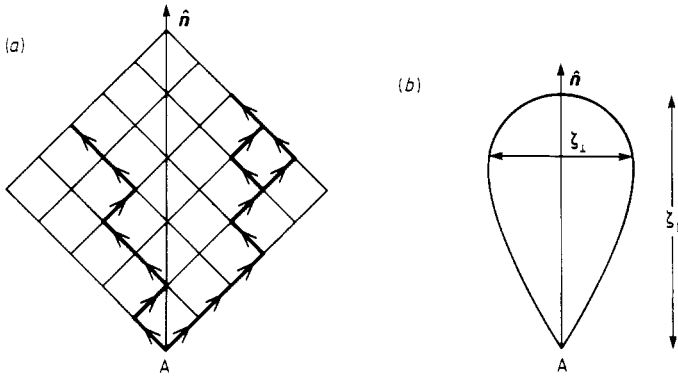
Figure 4. Directed percolation in two dimensions. (*a*) Directed lattice animal with root at A. (*b*) Cluster shape, showing parallel and perpendicular correlation length, $\xi_\|$, $\xi_\perp$, respectively.

of each site. These are defined by

$$\hat{\psi}_i|\ldots n_i\ldots\rangle = n_i|\ldots n_i-1\ldots\rangle \tag{5.1a}$$

$$\hat{\sigma}_i|\ldots n_i\ldots\rangle = (1-n_i)|\ldots n_i+1\ldots\rangle \tag{5.1b}$$

$$n_i = 0, 1. \tag{5.1c}$$

These operators satisfy the anticommutation relation

$$\hat{\psi}_i\hat{\sigma}_i + \hat{\sigma}_i\hat{\psi}_i = 1 \qquad [\hat{\psi}_i, \hat{\sigma}_j] = [\hat{\psi}_i, \hat{\psi}_j] = [\hat{\sigma}_i, \hat{\sigma}_j] = 0, \qquad i \neq j \tag{5.2}$$

and also

$$\hat{\sigma}_i^2 = \hat{\psi}_i^2 = 0. \tag{5.3}$$

Note that there are no powers of -1 in (5.1), reflecting the fact that there is no classical analogue of an antisymmetric wavefunction. We find that the analogue of (3.6) implies

$$\hat{\sigma}_i = \hat{\psi}_i^+ \tag{5.4}$$

and

$$\rho_k(x_1\ldots x_k; \Psi) = \langle 0|\hat{\psi}(x_1)\ldots\hat{\psi}(x_k)\prod_i(1+\hat{\psi}(x_i))|\Psi\rangle \tag{5.5}$$

using (3.39) and (5.3). The Liouvillian of this discrete GBM accounts for the following elementary processes:
  (1) Particles may evaporate with rate k.
  (2) Particles create offspring particles in neighbouring sites at a rate c.
  (3) Particles nucleate on sites at a rate μ.
The Liouvillian is then the sum over sites i of $\hat{L}_i$:

$$\hat{L} = \sum_{\text{sites}} \hat{L}_i(\mu, c, k) \tag{5.6a}$$

$$\hat{L}_i = \mu(1-\hat{\psi}_i)\hat{\psi}_i^+ + \tfrac{1}{2}c\sum_{\text{neighbours}}(1-\hat{\psi}_j)\hat{\psi}_j^+\hat{\psi}_i^+\hat{\psi}_i + k(1-\hat{\psi}_i^+)\hat{\psi}_i. \tag{5.6b}$$

In the appendix it is shown that this Liouvillian describes the quantum spin model in an external field used by Amati *et al* (1976) and Brower *et al* (1977) to study the dynamical vacuum instability of RFT. They showed that this indeed has a second-order phase transition, and that this is a consequence of the theory possessing a degenerate vacuum state. The action of a field operator (a nucleation event) generates a disturbance which propagates in space with a definite velocity. The disturbance acts as a front between the vacua, corresponding to the propagation of a kink or antikink along the substrate.

Acknowledgments

Appendix

To demonstrate the equivalence of equation (5.6) with the quantum spin model of RFT, consider the time development of equation (5.5), in the representation defined by equation (3.5). Letting

$$\hat{M} = \prod_i (1 + \hat{\psi}(x_i)), \qquad \hat{M}^{-1} = \prod_i (1 - \hat{\psi}(x_i)) \tag{A1}$$

we require

$$(\mathrm{d}/\mathrm{d}t)\hat{M}|\Psi\rangle = \hat{M}\hat{L}|\Psi\rangle = \hat{M}\hat{L}\hat{M}^{-1}\hat{M}|\Psi\rangle \tag{A2}$$

showing that the states $|\Psi\rangle$ are evolved by the Liouvillian

$$\hat{\mathscr{L}}_i = \hat{M}\hat{L}\hat{M}^{-1} = \mu\hat{\psi}_i^+(1 - \hat{\psi}_i) + \tfrac{1}{2}c\sum_{\text{neighbours}} \hat{\psi}_i^+(1 - \hat{\psi}_i)(\hat{\psi}_j^+ + 1)\hat{\psi}_j - k\hat{\psi}_i^+\hat{\psi}_i. \tag{A3}$$

The ψ fields can now be identified with the operators $\hat{\sigma}_z$, $\hat{\sigma}_\psi$, and $\hat{\sigma}_{\bar{\psi}}$ of the quantum spin model of Brower *et al* (1977) through the relations

$$\hat{\psi}_i^+\hat{\psi}_i \rightarrow \tfrac{1}{2}(1 - \hat{\sigma}_z^i)$$
$$\hat{\psi}_i^+\hat{\psi}_i - \hat{\psi}_i^+ \rightarrow \hat{\sigma}_{\bar{\psi}}^i \tag{A4}$$
$$\hat{\psi}_i^+\hat{\psi}_i + \hat{\psi}_i \rightarrow \hat{\sigma}_\psi^i$$

leading to the Hamiltonian

$$\hat{H} = -\hat{\mathscr{L}} = \tfrac{1}{2}k\sum_i (1 - \hat{\sigma}_z^i) - \tfrac{1}{2}c\sum_{\langle ij\rangle} \hat{\sigma}_{\bar{\psi}}^i\hat{\sigma}_\psi^j + \mu\sum_i \hat{\sigma}_{\bar{\psi}}^i. \tag{A5}$$

An essential difference between (A5) and the Hamiltonian used by Brower *et al* (1977) is that the nucleation rate acts as an external field, implying that the second-order phase transition is destroyed when $\mu > 0$.

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