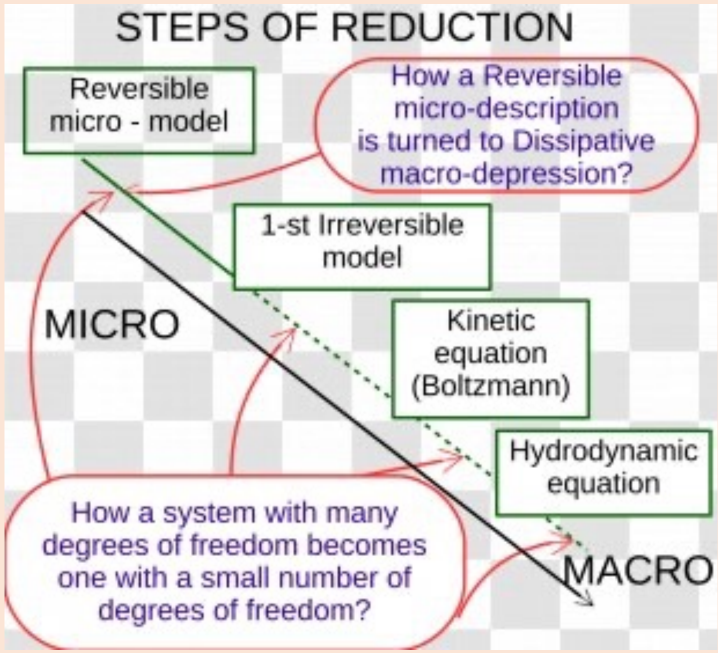
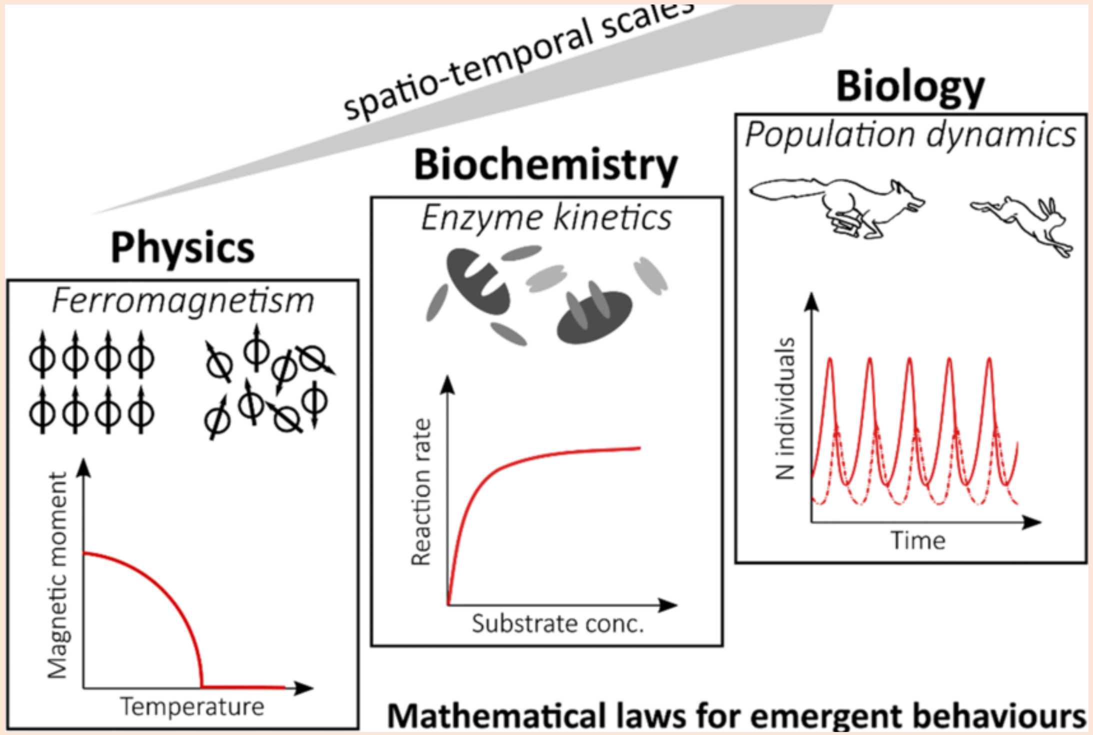
A kinetic view of Statistical Physics



Emergence over the length scales



Emergence of the Physical laws

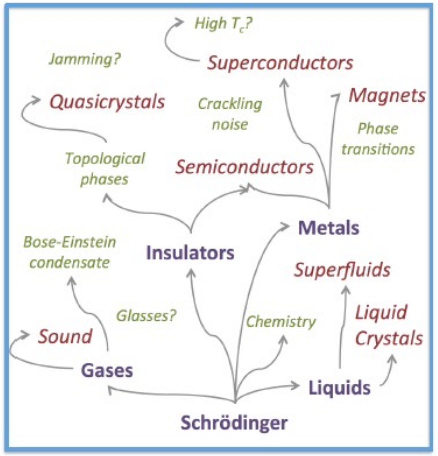


Fig. 1.2 Emergent. New laws describing macroscopic materials emerge from complicated microscopic behavior [47].

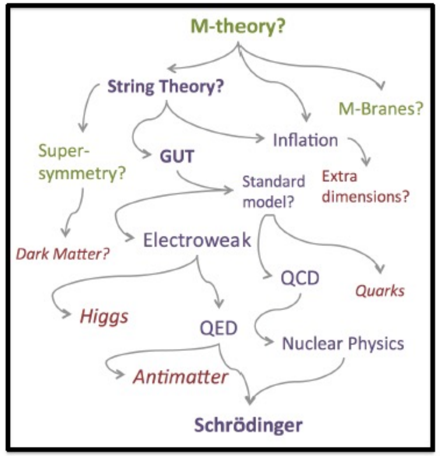
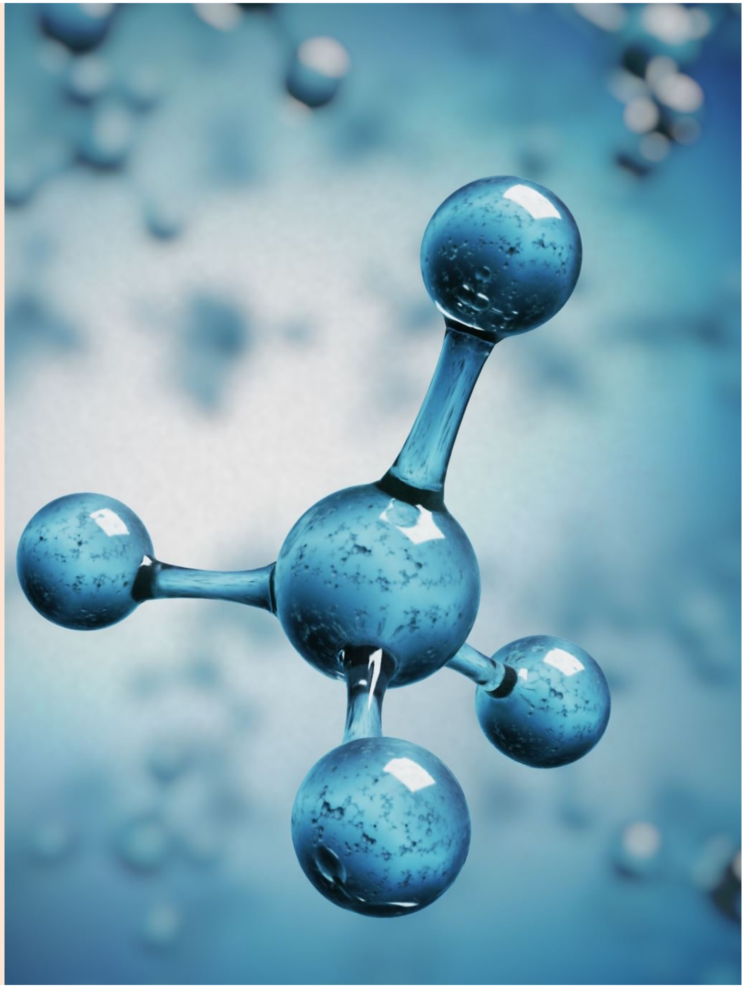


Fig. 1.3 Fundamental. Laws describing physics at lower energy emerge from more fundamental laws at higher energy [47].

Many particle systems

Many-particle systems often admit an (analytical) statistical description when their number becomes large.

In that sense they are simpler than few-particle systems. This feature has several diferent names – the law of large numbers, ergodicity, etc. – and it is one of the reasons for the spectacular successes of statistical physics.



Non-equilibrium Statistical Physics

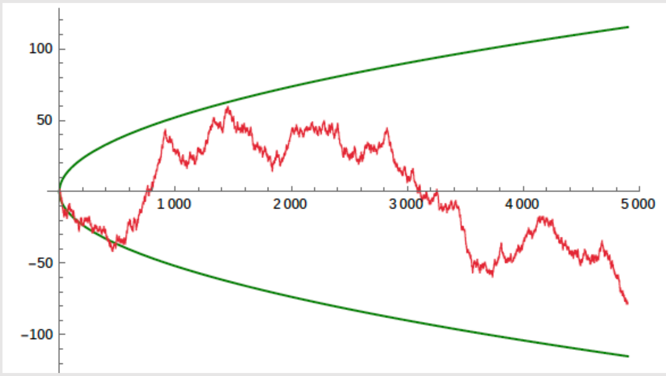
- there are no basic equations (like Maxwell equations in electrodynamics or Navier–Stokes equations in hydrodynamics) from which the rest follows;
- it is intermediate between fundamental and applied physics;
- common underlying techniques and concepts exist in spite of the wide diversity of the field;
- it naturally leads to the creation of methods that are useful in applications outside of physics (for example the Monte Carlo method and simulated annealing).

Diffusion

For the symmetric diffusion on a line, the probability density, the Prob [particle ∈ (x, x + dx)] ≡ P(x, t) dx satisfies the diffusion equation:

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}.$$

As we discuss soon, this equation describes the continuum limit of an unbiased random walk. The diffusion equation must be supplemented by an initial condition that we take to be P(x, 0) = δ(x), corresponding to a walk that starts at the origin.



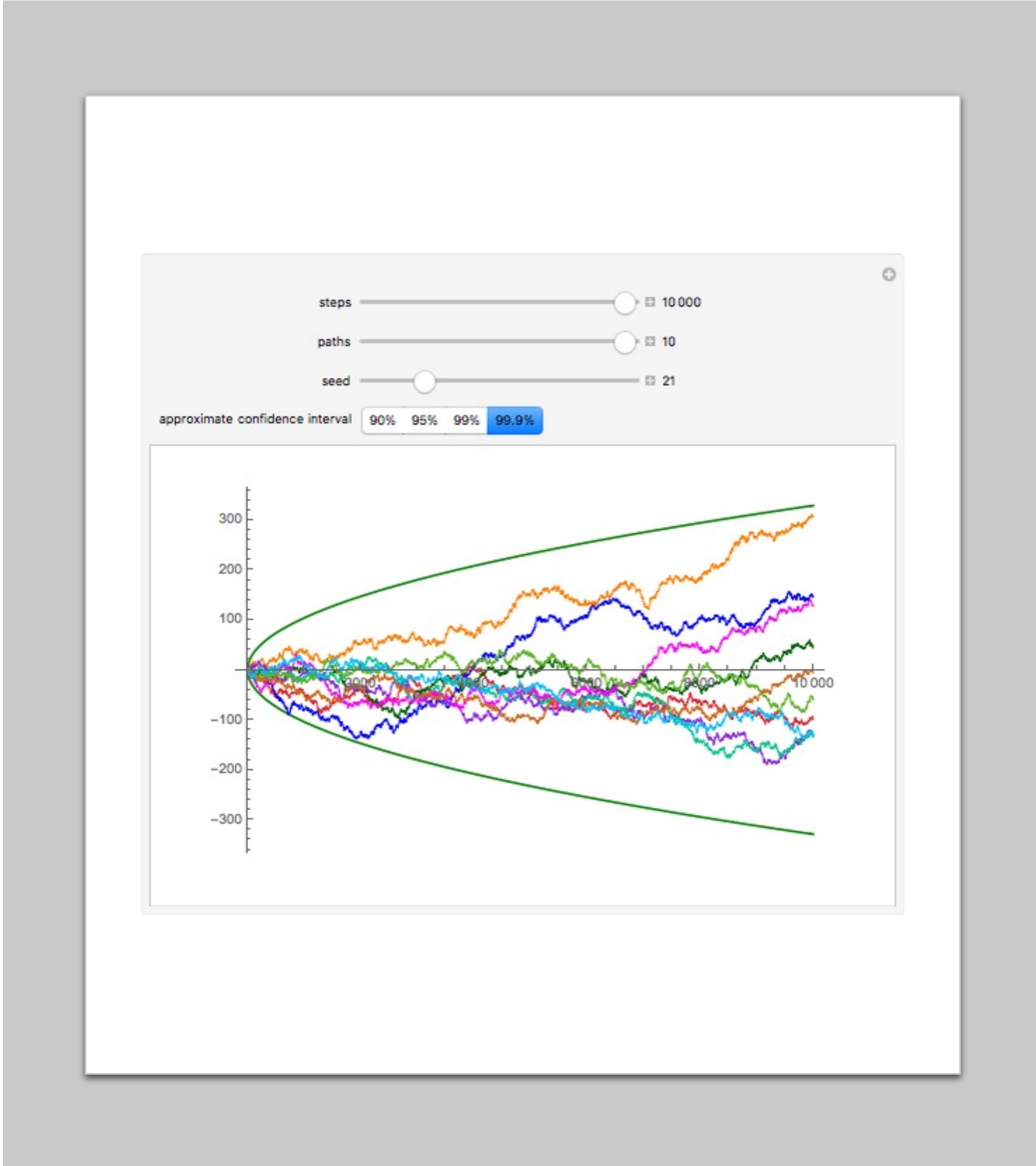
The confidence intervals can be obtained from the following result.

- Let s_n be the position of the walk at step n.
- The probability that s_n is greater than $x\sqrt{n}$ approaches, as n approaches infinity, the probability that the standard normal variable is greater than x; see [1], p. 76.

[1] W. Feller, An Introduction to Probability and Its Applications, vol. 1, 3rd ed., revised printing, New York: Wiley, 1968.

[2] H. Ruskeepää, Mathematica Navigator: Mathematics, Statistics, and Graphics, 3rd ed., San Diego, CA: Elsevier Academic Press, 2009.

https://demonstrations.wolfram.com/SimulatingTheSimpleRandomWalk/



Dimensional analysis

What is the mean displacement x? There is no bias, so clearly

$$\langle x \rangle \equiv \int_{-\infty}^{\infty} x\, P(x,t)\, dx = 0\,.$$

The next moment, the mean-square displacement,

$$\langle x^2 \rangle \equiv \int_{-\infty}^{\infty} x^2\, P(x,t)\, dx$$

is non-trivial. Obviously, it should depend on the diffusion coefficient D and time t. We now apply dimensional analysis to determine these dependences. If L denotes the unit of length and T denotes the time unit, then from (1.2) the dimensions of $\langle x^2 \rangle, D$, and t are

$$[\langle x^2 \rangle] = L^2\,, \quad [D] = L^2/T\,, \quad [t] = T\,.$$

The only quantities with units of length squared that can be formed from these parameters are the mean-square displacement itself and the product Dt. Hence

$$\langle x^2 \rangle = C \times Dt. \tag{1.3}$$

Scaling

Let's now apply dimensional analysis to the probability density P(x,t|D); Since [P] = L^{-1}, √Dt P(x, t|D) is dimensionless, so it must depend on dimensionless quantities only. From variables x, t, D we can form a single dimensionless quantity x/√Dt

$$P(x,t) = \frac{1}{\sqrt{Dt}}\mathcal{P}(\xi)\,, \qquad \xi = \frac{x}{\sqrt{Dt}}\,.$$

For the diffusion equation, substituting in the scaling ansatz reduces this PDE to the ODE

$$2\mathcal{P}'' + \xi\mathcal{P}' + \mathcal{P} = 0\,.$$

Integrating twice and invoking both symmetry ($\mathcal{P}'(0) = 0$) and normalization, we obtain $\mathcal{P} = (4\pi)^{-1/2}\, e^{-\xi^2/4}$, and finally the Gaussian probability distribution

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\exp\left[-\frac{x^2}{4Dt}\right]. \qquad (1.5)$$

Asymptotic scaling

For the diffusion equation with an initial condition on a finite domain rather than a point, scaling holds only in the limit $x, t \to \infty$, with the scaling variable ξ kept finite.

Renormalization

The strategy of the renormalization group method is to understand the behavior on large "scales" – here meaning long times – by iterating the properties of random walks on smaller time scales. For the diffusion equation, we start with the identity

$$P(x, 2t) = \int_{-\infty}^{\infty} P(y, t)\, P(x - y, t)\, dy,$$

Mathematically, the probability distribution after time 2t is given by the convolution of probability distributions to reach the intermediate time t and the probability distribution to propagate from time t to 2t.

Renormalization

The convolution form of Eq. (1.6) calls out for applying the Fourier transform,

$$P(k,t) = \int_{-\infty}^{\infty} e^{ikx}\, P(x,t)\, dx\,, \tag{1.7}$$

that recasts (1.6) into the algebraic relation $P(k,2t) = [P(k,t)]^2$. The scaling form (1.4) shows that $P(k,t) = \mathcal{P}(\kappa)$ with $\kappa = k\sqrt{Dt}$, so the renormalization group equation is

$$\mathcal{P}(\sqrt{2}\,\kappa) = [\mathcal{P}(\kappa)]^2\,.$$

Taking logarithms and defining $z \equiv \kappa^2, Q(z) \equiv \ln \mathcal{P}(\kappa)$, we arrive at $Q(2z) = 2Q(z)$, whose solution is $Q(z) = -Cz$, or $P(k,t) = e^{-2k^2 Dt}$. (The constant $C = 2$ may be found, e.g. by expanding (1.7) for small k, $P(k,t) = 1 - k^2\langle x^2\rangle$, and recalling that $\langle x^2\rangle = 2Dt$.) Performing the inverse Fourier transform we recover (1.5). Thus the Gaussian probability distribution represents an exact solution to a renormalization group equation. This derivation shows that the renormalization group is ultimately related to scaling.

Master equation

The symmetric random walk on a 1d lattice has a probability that evolves as

$$\frac{\partial P_n}{\partial t} = P_{n-1} + P_{n+1} - 2P_n \, .$$

The first two terms on the right account for the increase in P_n because of a hop from n − 1 to n or because of a hop from n + 1 to n, respectively. Similarly, the last term accounts for the decrease of P_n because of hopping from n to n +/- 1.

Program

2 Diffusion/Reaction

3 Aggregation

4 Fragmentation

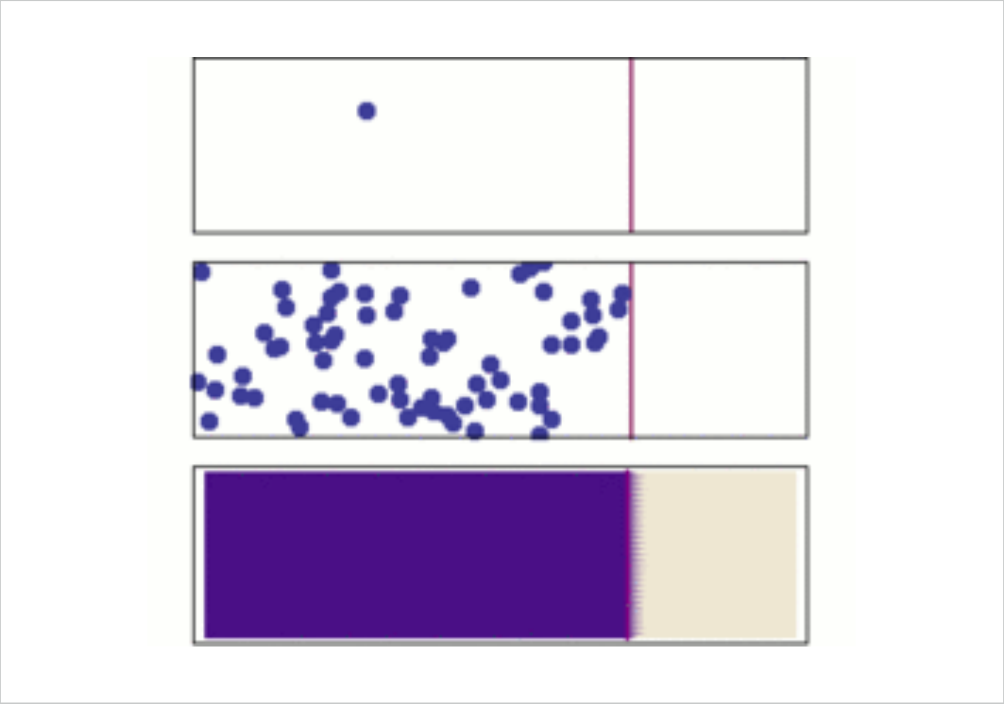
5 Adsorption (definition only)

6 Spin Dynamics

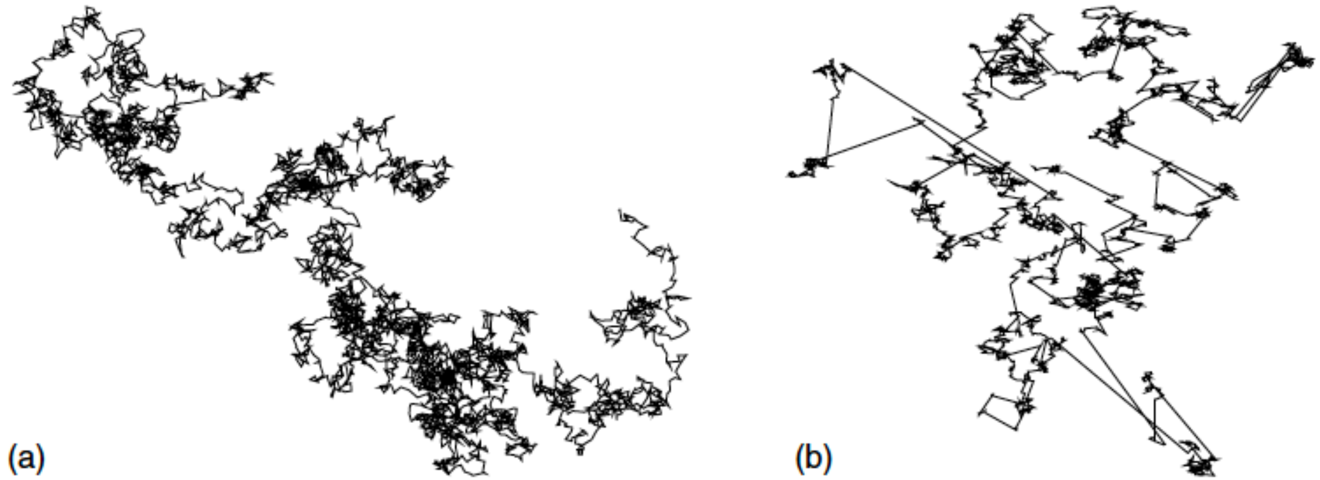
7 Coarsening

2 Diffusion

https://en.wikipedia.org/wiki/Diffusion

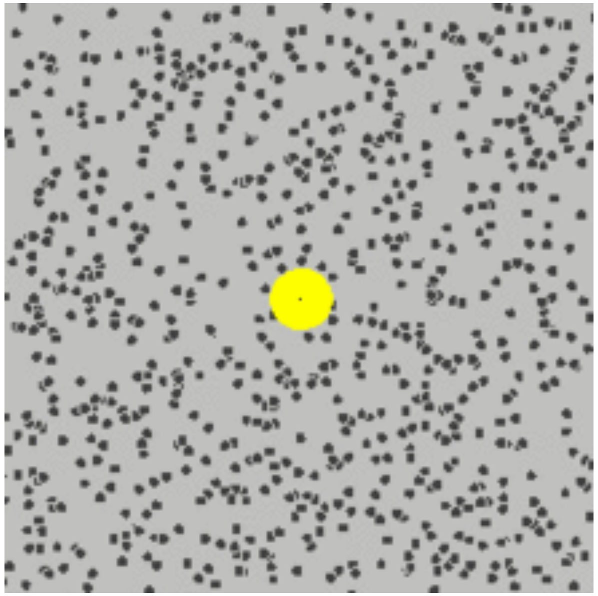


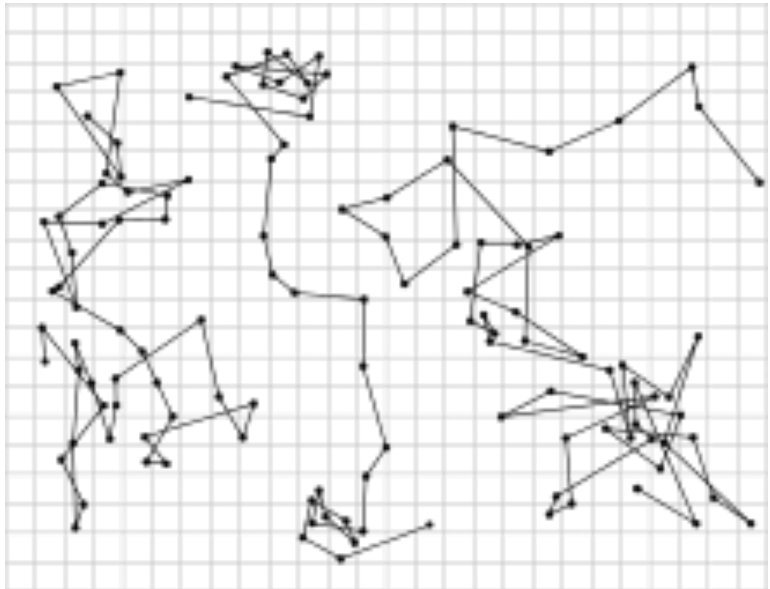
Random walk



Brownian Motion

https://en.wikipedia.org/wiki/Brownian_motion





1d Probability: discrete step & time RW

At each step, the walker moves a unit distance to the right with probability p or a unit distance to the left with probability $q = 1 - p$. The probability $P_N(x)$ that the walk is at x at the N^{th} step obeys

$$P_N(x) = pP_{N-1}(x-1) + qP_{N-1}(x+1)\,.$$

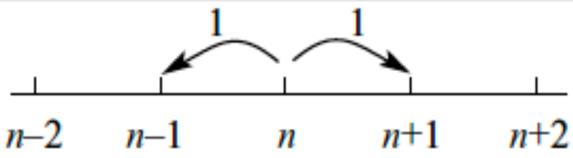
Notice that the probability $\Pi_N(r)$ that the walk takes r steps to the right and $N - r$ to the left has the binomial form

$$\Pi_N(r) = \binom{N}{r} p^r q^{N-r}\,.$$

If the random walk starts at the origin, the total displacement will be $x = 2r - N$.
Using Stirling's approximation for large N to simplify the binomial distribution we find (check errata 2 -> 8)

$$P_N(x) \to \frac{1}{\sqrt{\underset{8}{\cancel{2}}\pi Npq}}\, e^{-[x-N(p-q)]^2/\underset{8}{\cancel{2}}Npq}\,.$$

Continuous time RW



Master equation

$$\frac{\partial P_n}{\partial t} = P_{n+1} - 2P_n + P_{n-1} \; .$$

$$P_n(t) = I_n(2t)\, e^{-2t} \; ,$$

$$P_n(t) \to \frac{1}{\sqrt{4\pi t}}\, e^{-n^2/4t} \; .$$

Continuous space n -> x. Taylor expanding the Master equation, we find the diffusion eq.

$$\frac{\partial P(x,t)}{\partial t} = D\, \frac{\partial^2 P(x,t)}{\partial x^2},$$

Solve using FT

$$P(k,t) = \int_{-\infty}^{\infty} P(x,t)\, e^{ikx}\, dx, \qquad P(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} P(k,t)\, e^{-ikx}\, dk \; .$$

$$\frac{\partial P(k,t)}{\partial t} = -Dk^2\, P(k,t),$$

$$P(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-Dk^2 t}\, e^{-ikx}\, dk = \frac{1}{\sqrt{4\pi D t}}\, e^{-x^2/4Dt},$$

The Langevin approach

To illustrate the Langevin approach, let's begin with diffusive motion in one dimension.[15] We mimic the effect of collisions by a stochastic noise $\xi(t)$. The equation of motion for the position $x(t)$ of the particle,

$$\frac{dx}{dt} = \xi(t), \tag{2.90}$$

is a *stochastic differential equation* because $\xi(t)$ is a stochastic variable that is different for each realization of the noise. This noise has the following basic properties:

- $\xi(t)$ is independent of x.
- $\xi(t)$ fluctuates on microscopically short time scales to mimic the effect of collisions.[16]

[15] The same treatment works in higher dimensions; we focus on one dimension for simplicity.

[16] For pollen grains, the objects of the experiments by Robert Brown, their linear dimension is of the order of 10^{-5} m and there are of the order of 10^{20} collisions per second. It is clearly impossible (and pointless!) to follow the collisional changes on this incredibly short 10^{-20} s time scale.

The Langevin approach

- $\langle \xi(t) \rangle = 0$ so that collisions do not conspire to give a net velocity (the bracket $\langle \cdots \rangle$ denotes averaging over different realizations of noise).
- There is no correlation between the noise at different times, $\langle \xi(t)\xi(t') \rangle = 2D\delta(t - t')$; we will justify the amplitude $2D$ subsequently.

Integrating Eq. (2.90) yields the formal solution

$$x(t) = \int_0^t \xi(t')\, dt'. \tag{2.91}$$

When we average (2.91) over the noise we obtain $\langle x(t) \rangle = 0$ because $\langle \xi(t) \rangle = 0$. Squaring Eq. (2.91) gives

$$\langle x^2 \rangle = \int_0^t \int_0^t \langle \xi(t')\xi(t'') \rangle\, dt'\, dt''. \tag{2.92}$$

The Langevin approach

Using $\langle \xi(t')\xi(t'')\rangle = 2D\delta(t'-t'')$, we find $\langle x^2\rangle = 2Dt$, which reproduces the result from the diffusion equation. This connection with diffusion justifies the amplitude $2D$ in the noise correlation function. Notice that the time dependence follows from Eq. (2.90) by dimensional analysis. Since $\delta(t)$ has units of $1/t$ (because the integral $\int \delta(t)\,dt = 1$), the statement $\langle \xi(t)\xi(t')\rangle = 2D\delta(t-t')$ means that ξ has the units $\sqrt{D/t}$. Thus from Eq. (2.91) we see that $x(t)$ must have units of $\sqrt{Dt}$.

Not only is the variance identical to the prediction of the diffusion equation, the entire probability distribution is Gaussian. This fact can be seen by dividing the interval $(0,t)$ into the large number $t/\Delta t$ of sub-intervals of duration Δt, replacing the integral in Eq. (2.91) by the sum

$$x(t) = \sum_{j=1}^{t/\Delta t} \zeta_j\,, \qquad \zeta_j = \int_{(j-1)\Delta t}^{j\Delta t} \xi(t')\,dt', \tag{2.93}$$

and noting that the displacements ζ_j are independent identically distributed random variables satisfying $\langle \zeta_j\rangle = 0$, $\langle \zeta_j^2\rangle = 2D\Delta t$. Therefore we apply the central limit theorem to obtain

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}\, e^{-x^2/4Dt}\,. \tag{2.94}$$

The Langevin equation

The Gaussian probability distribution is particularly striking in view of the feature that the Langevin equation (2.90) builds in an unphysical infinite velocity. Indeed, in a small time interval Δt, the mean-square displacement of a Brownian particle is $\langle \Delta x^2 \rangle = 2D\Delta t$. Therefore the typical velocity $v_{\mathrm{typ}} \sim \Delta x/\Delta t \sim \sqrt{D/\Delta t}$ diverges as $\Delta t \to 0$. Mathematically, the function $x(t)$ is continuous but nowhere differentiable. Langevin proposed the equation

$$\frac{d\mathbf{v}}{dt} = -\gamma \mathbf{v} + \boldsymbol{\xi}(t), \qquad \frac{d\mathbf{x}}{dt} = \mathbf{v}, \tag{2.95}$$

with the velocity $\mathbf{v}$, which remains finite, as the basic variable.[17] The Langevin approach (2.95) posits that the influence of the fluid can be divided into a systematic frictional force, as represented by the term $-\gamma\mathbf{v}$, and a fluctuating term represented by $\boldsymbol{\xi}(t)$. The frictional force is normally governed by Stokes' law[18] in which $\gamma = 6\pi a\eta/m$, where a is the particle radius (assumed spherical), η the viscosity coefficient of the fluid, and m the mass of the Brownian particle. The noise has zero mean value and the correlation function $\langle \xi_i(t)\xi_j(t')\rangle = \Gamma\delta_{ij}\,\delta(t-t')$. Since both these contributions are caused by the surrounding fluid, they are not independent; we shall see that γ and Γ are connected by a *fluctuation–dissipation relation*.

$$\mathbf{v}(t) = \mathbf{v}_0\, e^{-\gamma t} + e^{-\gamma t} \int_0^t \boldsymbol{\xi}(t')\, e^{\gamma t'}\, dt' \,. \tag{2.96}$$

Therefore the average velocity decays exponentially: $\langle \mathbf{v} \rangle = \mathbf{v}_0\, e^{-\gamma t}$. The mean-square velocity exhibits a more interesting behavior:

$$\begin{aligned} \langle \mathbf{v}^2 \rangle &= \mathbf{v}_0^2\, e^{-2\gamma t} + e^{-2\gamma t} \int_0^t \int_0^t \langle \boldsymbol{\xi}(t')\, \boldsymbol{\xi}(t'') \rangle e^{\gamma (t'+t'')} dt'\, dt'' \\ &= \mathbf{v}_0^2\, e^{-2\gamma t} + \frac{3\Gamma}{2\gamma} \left(1 - e^{-2\gamma t}\right) . \end{aligned} \tag{2.97}$$

The equipartition theorem tells us that in equilibrium each degree of freedom has an average energy $T/2$. (We always measure the temperature in energy units; equivalently, we set Boltzmann's constant $k = 1$.) Hence $\langle \mathbf{v}^2 \rangle = 3T/m$ in three dimensions. By comparing with Eq. (2.97) in the limit $t \to \infty$, the friction coefficient and the noise amplitude are therefore related by the fluctuation–dissipation relation $\Gamma = 2T\gamma/m$.

To determine the probability distribution $P(\mathbf{v}, t \,|\, \mathbf{v}_0)$ from (2.96) we can proceed as in the derivation of (2.94) from (2.93), that is, we write

$$\mathbf{v}(t) - \mathbf{v}_0\, e^{-\gamma t} = \sum_{j=1}^{t/\Delta t} \boldsymbol{\zeta}_j \,, \quad \boldsymbol{\zeta}_j = e^{-\gamma t} \int_{(j-1)\Delta t}^{j\Delta t} \boldsymbol{\xi}(t')\, e^{\gamma t'}\, dt' \,. \tag{2.98}$$

On the right-hand side we have the sum of independent (albeit not identically distributed) random variables. The central limit theorem still holds in this case,[19] however, and taking the $\Delta t \to 0$ limit, we arrive at

$$P(\mathbf{v}, t \,|\, \mathbf{v}_0) = \left[\frac{m}{2\pi T(1-e^{-2\gamma t})}\right]^{3/2} \exp\left[-\frac{m(\mathbf{v}-\mathbf{v}_0\, e^{-\gamma t})^2}{2T(1-e^{-2\gamma t})}\right], \tag{2.99}$$

which approaches the Maxwellian distribution in the $t \to \infty$ limit.

[17] From Eq. (2.95), the velocity is continuous but nowhere differentiable, so the acceleration is infinite. Note also that in the $\gamma \to \infty$ limit, we can ignore the inertia term $\dot{\mathbf{v}}$ and recover (2.90).

[18] The drag force is linear in velocity when velocity is small, or fluid is very viscous. More precisely, the dimensionless Reynolds number (that gives the ratio of inertial to viscous terms) should be small. For a sphere, the Reynolds number is $Re = \rho v a/\eta$.

[19] The full variance is the sum of individuals variances $\sum_{j=1}^{t/\Delta t} \left\langle \zeta_j^2 \right\rangle$.

Our original goal was to describe the probability distribution of the displacement, so let's now examine this quantity. Integrating $\dot{\mathbf{x}} = \mathbf{v}$ we obtain

$$\mathbf{x}(t) = \mathbf{x}_0 + \gamma^{-1}\mathbf{v}_0(1 - e^{-\gamma t}) + \gamma^{-1} \int_0^t \boldsymbol{\xi}(t') \left[1 - e^{-\gamma(t-t')}\right] dt' , \tag{2.100}$$

so that the average displacement is $\langle \mathbf{x} \rangle = \mathbf{x}_0 + \gamma^{-1}\mathbf{v}_0(1 - e^{-\gamma t})$. Squaring (2.100) we find the mean-square displacement

$$\begin{aligned} \langle \mathbf{x}^2 \rangle &= \mathbf{x}_0^2 + \gamma^{-2}\mathbf{v}_0^2 \, \overset{(1-e^{-\gamma t})^2}{\cancel{e^{-2\gamma t}}} + 2\gamma^{-1}(1 - e^{-\gamma t})\mathbf{x}_0 \cdot \mathbf{v}_0 + \frac{3\Gamma}{2\gamma^3}\, g(t), \\ g(t) &= 2\gamma t - 3 + 4e^{-\gamma t} - e^{-2\gamma t} . \end{aligned} \tag{2.101}$$

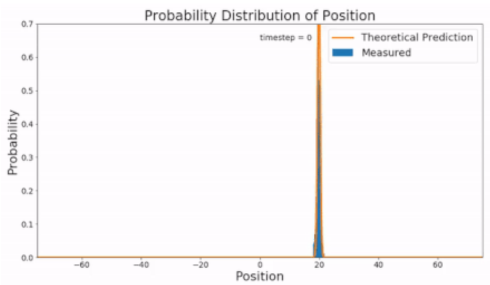
With a bit more work we obtain the entire distribution

$$P(\mathbf{x}, \mathbf{v}, t \,|\, \mathbf{x}_0, \mathbf{v}_0) = \left[\frac{m\gamma^2}{2\pi T g(t)}\right]^{3/2} \exp\left[-\frac{m\gamma^2[\mathbf{x} - \mathbf{x}_0 - \mathbf{v}_0(1 - e^{-\gamma t})/\gamma]^2}{2Tg(t)}\right]. \tag{2.102}$$

Asymptotically this probability distribution agrees with the solution to the diffusion equation when the diffusion constant is given by

$$D = \frac{T}{m\gamma} = \frac{T}{6\pi \eta a} . \tag{2.103}$$

Fokker-Planck



https://en.wikipedia.org/wiki/Fokker–Planck_equation

There exists a standard prescription to go from a Langevin equation for a stochastic variable x to the *Fokker–Planck* equation for the probability distribution of this variable $P(x,t)$. Because this connection is extensively discussed in standard texts, we do not treat this subject here. We merely point out that for the generic Langevin equation

$$\frac{dx}{dt} = F(x) + \xi(t),$$

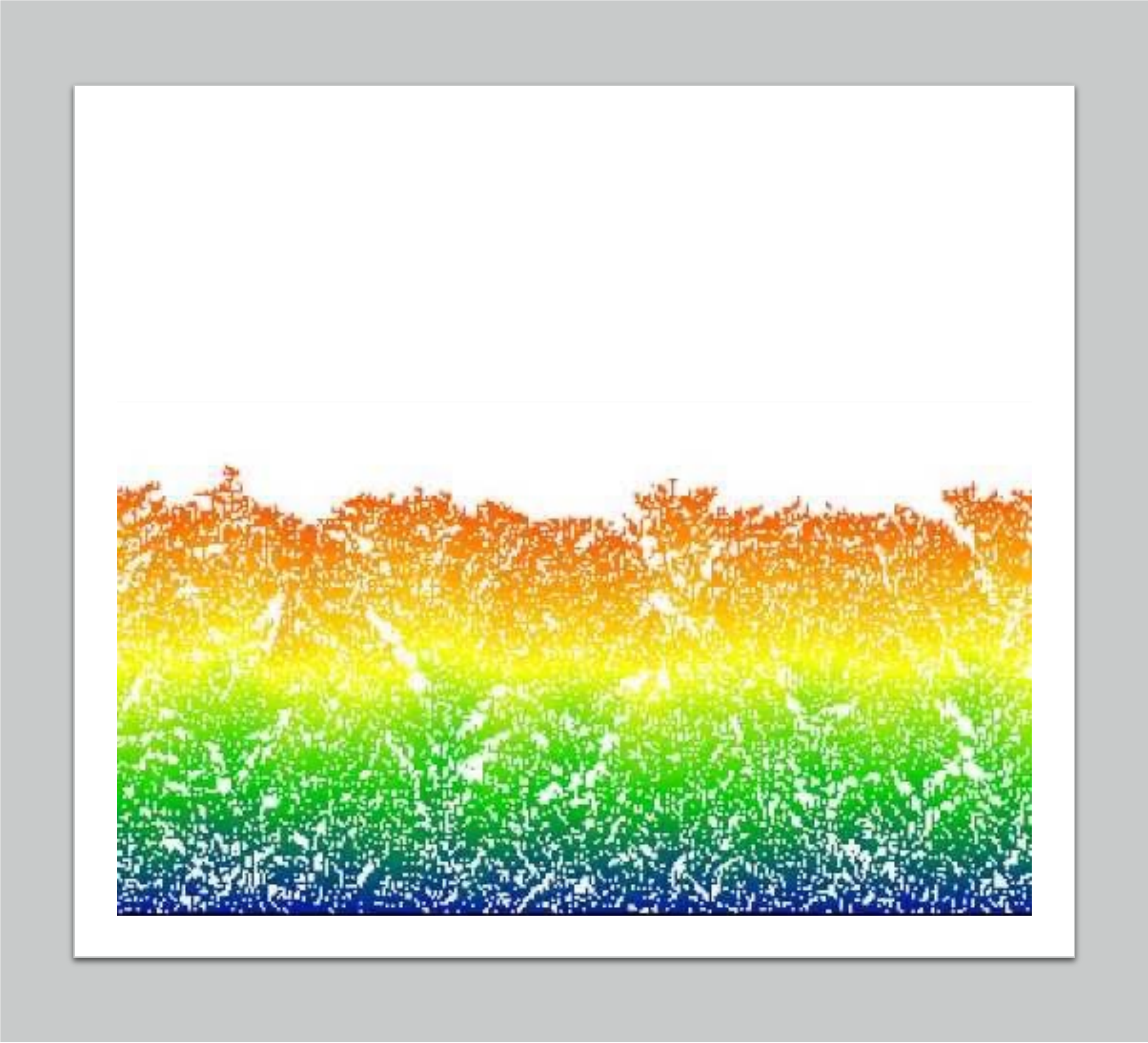
in which the noise $\xi(t)$ has zero mean and no correlations, $\langle \xi \rangle = 0$ and $\langle \xi(t)\,\xi(t') \rangle = 2\Gamma\,\delta(t-t')$, the corresponding Fokker–Planck equation for $P(x,t)$ is

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left[F(x)\,P\right] + \Gamma\,\frac{\partial^2 P}{\partial x^2}\,. \tag{2.104}$$

For example, for the Langevin equation $\dot{x} = \xi(t)$, the corresponding Fokker–Planck equation reduces to the standard diffusion equation (2.7). The salient feature of the Fokker–Planck equation is that its solution always has a Gaussian form. We will exploit this property in our discussion in Section 12.3 about the small-fluctuation expansion of the master equation for reacting systems.

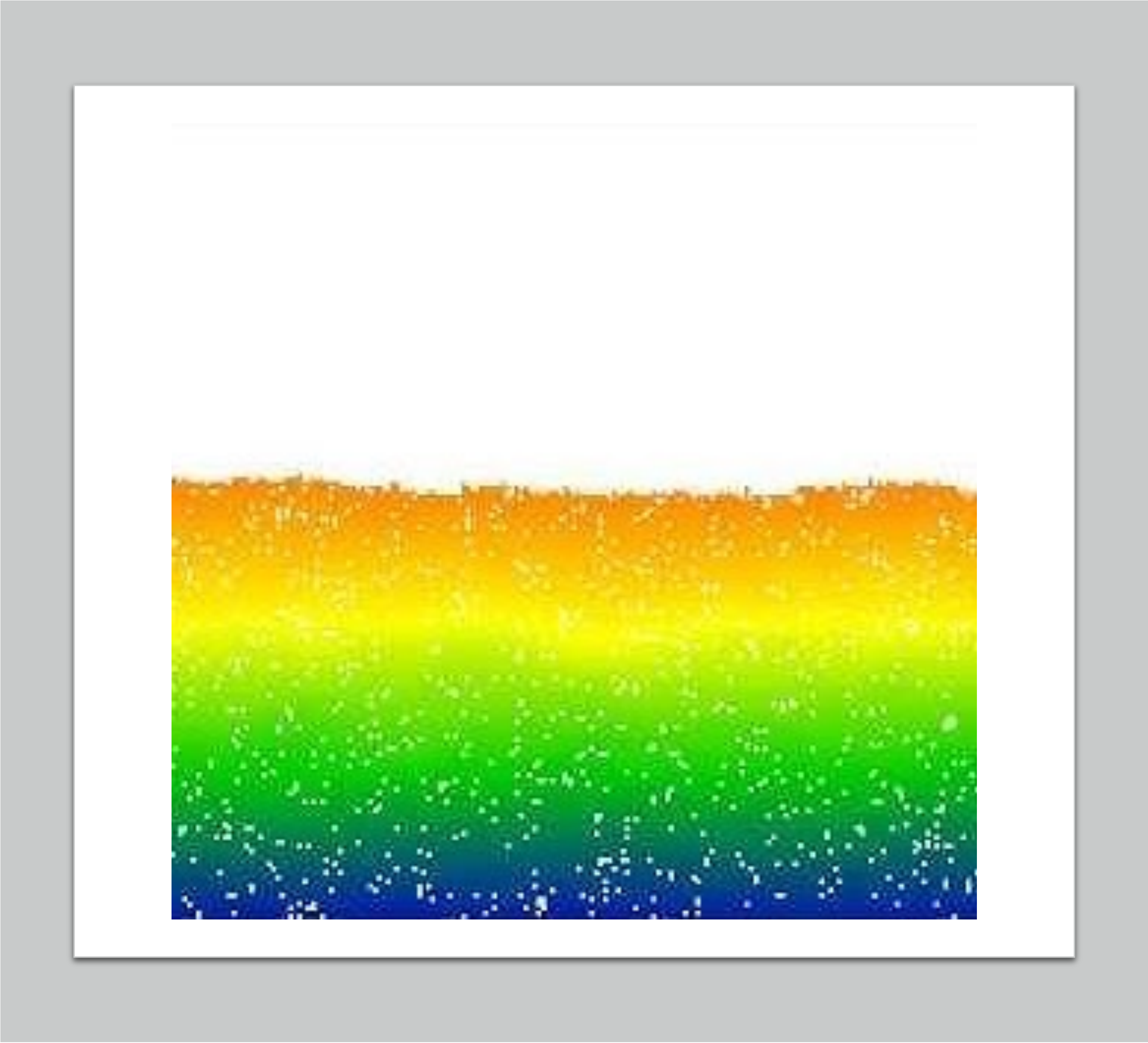
Surface growth

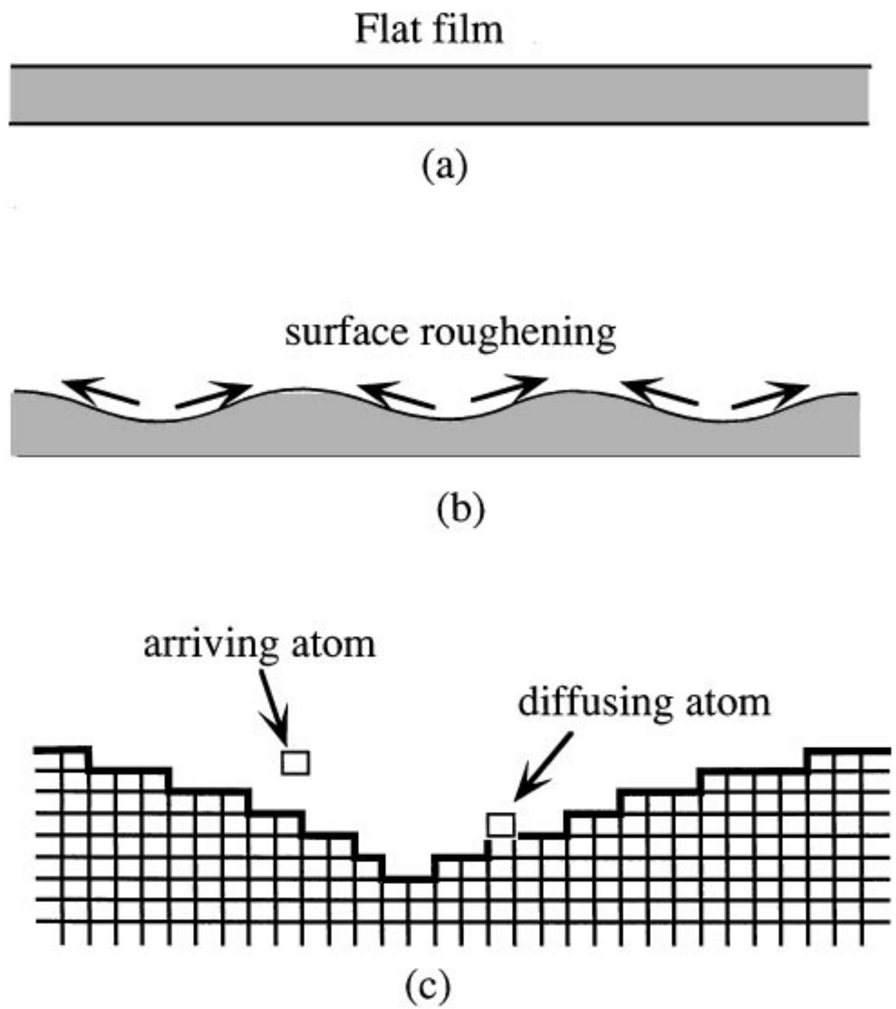
https://www.youtube.com/watch?v=sQQyvIdW2sc



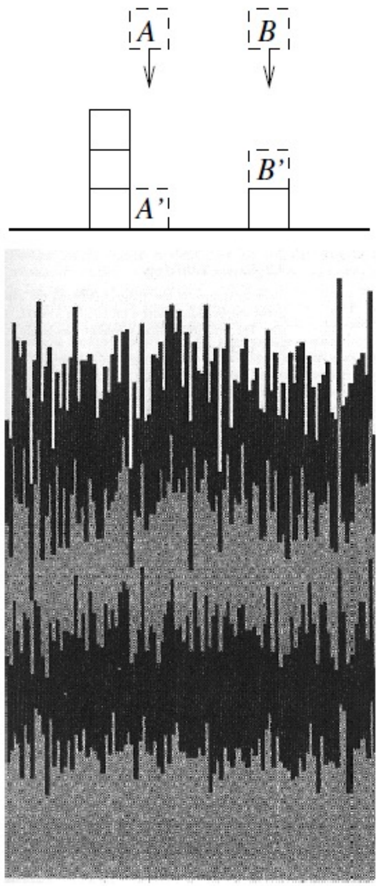
Surface growth

https://www.youtube.com/watch?v=xZfFwZYZOJ0

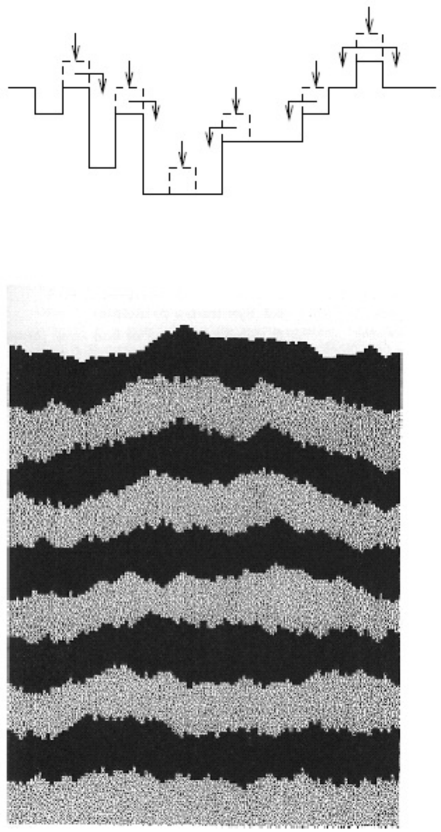



Flat film
(a)
surface roughening
(b)
arriving atom
diffusing atom
(c)

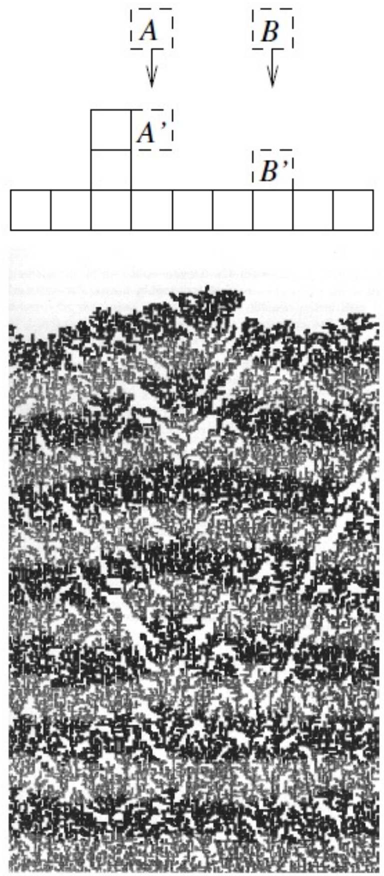
Random deposition



Random deposition with relaxation



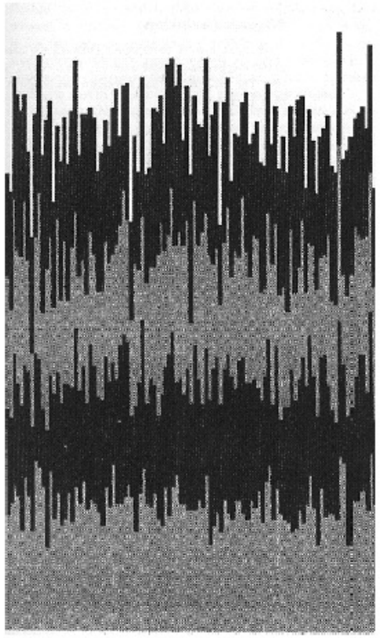
Ballistic deposition



Classical CLT

$\partial_t h = \eta(x,t)$

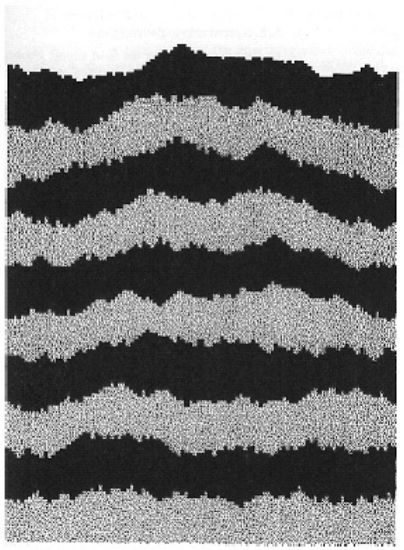
$t^{\frac{1}{2}}$ fluctuations



Edwards-Wilkinson eq.

$\partial_t h = \nu\, \partial_x^2 h + \eta(x,t)$

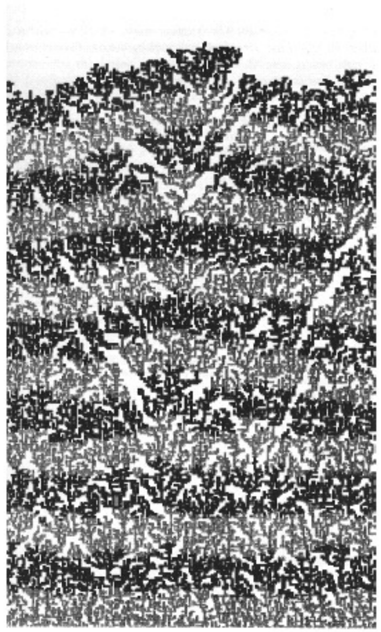
$t^{\frac{1}{4}}$ fluctuations



Kardar-Parisi-Zhang eq.

$\partial_t h = \nu\, \partial_x^2 h + \lambda(\partial_x h)^2 + \eta$

$t^{\frac{1}{3}}$ fluctuations



Generalizations

We want to understand how the behavior of a deterministic system changes when it interacts with its environment. We cannot describe the environment in a precise manner and instead we mimic its influence on the system as a stochastic force.

Generally Langevin equations are constructed by the following standard procedure:
1. Start with a deterministic equation. Usually it is an ordinary differential equation, but other choices (e.g. a difference equation) are also possible.
2. Add a noise term. In the simplest scenario, the noise is assumed to be independent of the underlying variable, temporarily uncorrelated, and Gaussian.

An ambitious generalization of the Langevin program is to start with a deterministic partial differential equation. The most important linear partial differential equation is the diffusion equation. The most prominent nonlinear generalization to the diffusion equation is the Burgers equation.

Surface growth: Edwards-Wilkinson

The Edwards–Wilkinson (EW) equation is the diffusion equation with noise:

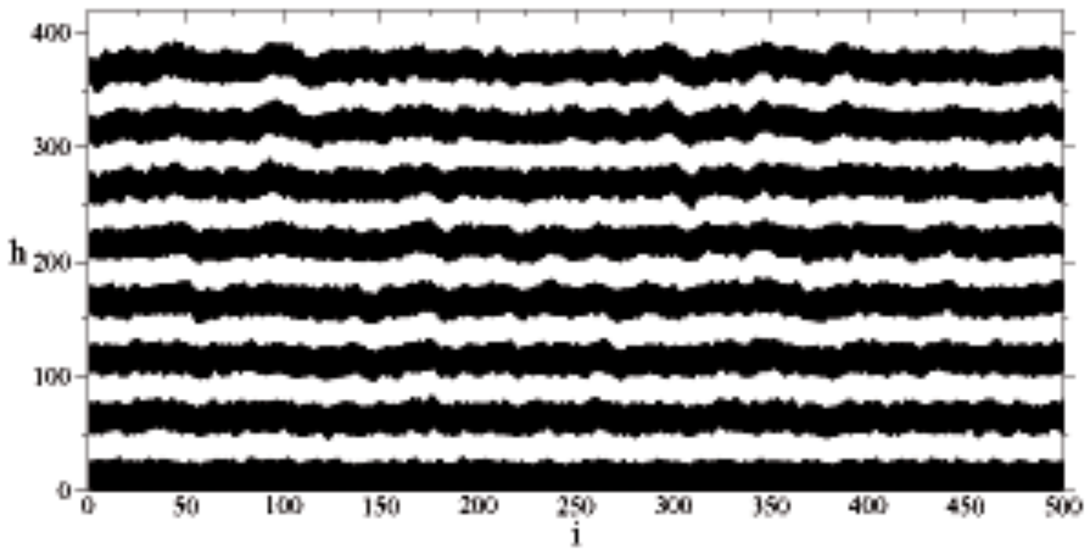
$$\frac{\partial h}{\partial t} = D\nabla^2 h + \eta \, .$$

This Langevin equation has been proposed as a model of surface growth where atoms from an external source are deposited onto a surface and adsorbed atoms can evaporate.
Depending on the nature of the incident flux, the mobility of the adatoms, and relaxation mechanisms, a wide variety of surface morphologies can arise.

A surface is characterized by its height, H(r, t), as a function of transverse coordinates r and time t. It is more conveniente to consider deviations of the surface from its average height, h(r, t) = H(r, t) – <H>.
A basic goal is to understand the properties of the height function h and its correlation function <h(r, t)h(r’, t’)> .

Edwards-Wilkinson

$$\frac{\partial h}{\partial t} = D\nabla^2 h + \eta \,.$$



Edwards-Wilkinson

$$\frac{\partial h}{\partial t} = D\nabla^2 h + \eta\,.$$

Viewed as a surface evolution model, the Laplacian is positive near local surface minima (positive curvature) and negative near local maxima (negative curvature).
Thus the Laplacian tends to smooth a surface and mimics the influence of the surface tension.
The noise is assumed to be Gaussian with zero mean, independent of h, and spatially and temporarily uncorrelated. That is,

$$\langle \eta \rangle = 0, \qquad \langle \eta(\mathbf{x},t)\eta(\mathbf{x}',t') \rangle = 2\Gamma\delta(\mathbf{x}-\mathbf{x}')\,\delta(t-t')\,.$$

The competition between the effect of the noise and the Laplacian smoothing leads to a non-trivial surface morphology.

Edwards-Wilkinson (1d)

Let's compute the interface width $w(t) = \sqrt{\langle h^2(x,t)\rangle}$ for the one-dimensional situation with an initially flat interface, $h(x, t = 0) = 0$. As always, it is useful to start with dimensional analysis. By translational invariance, the width w is independent of x. Therefore $w = w(t, D, \Gamma)$. From (2.105) we find $[\eta] = L/T$, while (2.106) gives $[\Gamma] = [\eta]^2 LT = L^3/T$ (in one dimension). Thus dimensional analysis alone leads to a non-trivial scaling prediction

$$w^2 = Dt\,F(\kappa), \qquad \text{with} \quad \kappa = D^3 t/\Gamma^2, \tag{2.107}$$

for the width. We can do even better by exploiting the linearity of the EW equation (2.105). The height (and width) should be proportional to η, i.e. to $\sqrt{\Gamma}$, from (2.106). This dependence will certainly hold in the long-time limit, and is, in fact, valid for all times for an initially flat surface. Hence w is proportional to $\sqrt{\Gamma}$, implying that $F(\kappa) = C\kappa^{-1/2}$. Thus dimensional analysis and linearity determine the width

$$w^2 = C\Gamma\sqrt{t/D} \tag{2.108}$$

up to an amplitude C.

Edwards-Wilkinson (1d)

To derive (2.108) analytically and thereby compute the amplitude, we write the general solution of Eq. (2.105) in one dimension:

$$h(x,t) = \int_0^t dt_1 \int_{-\infty}^{\infty} dx_1 \, \frac{\eta(x_1,t_1)}{\sqrt{4\pi D(t-t_1)}} \, e^{-(x-x_1)^2/4D(t-t_1)} \, . \qquad (2.109)$$

That is, a noise input at (x_1, t_1) propagates to (x, t) via the Gaussian propagator of diffusion. Taking the square and averaging to obtain $w^2 = \langle h^2(x,t) \rangle$, we arrive at (2.108) with $C = \sqrt{2/\pi}$ (problem 2.28).

Edwards-Wilkinson (2d)

In two dimensions, dimensional analysis predicts

$$w^2 = Dt\,F(\kappa), \qquad \text{with} \quad \kappa = D^2 t/\Gamma\,. \tag{2.110}$$

Using this and the dependence $w \sim \sqrt{\Gamma}$ we arrive at the puzzling result that the width attains a stationary form: $w^2 = C\Gamma/D$. This stationarity is, in principle, feasible as the asymptotic behavior. However, owing to the lack of a characteristic time, the prediction $w^2 = C\Gamma/D$ (if correct!) would be valid at all times. This constancy is obviously impossible since we set the initial width equal to zero. (In fact, we shall see that the width is ill-defined, namely the computation of $w^2 = \langle h^2(\mathbf{x},t)\rangle$ with $h(\mathbf{x},t)$ given by (2.112), leads to $w = \infty$.)

To resolve this dilemma, let us look at the two-point correlation function

$$C(\mathbf{x},t) = \langle h(\mathbf{x},t)\,h(\mathbf{0},t)\rangle\,. \tag{2.111}$$

This function is well-defined and finite for $\mathbf{x} \neq \mathbf{0}$. To compute $C(\mathbf{x},t)$ we again use the general solution

$$h(\mathbf{x},t) = \int_0^t dt_1 \int d\mathbf{x}_1\, \frac{\eta(\mathbf{x}_1,t_1)}{4\pi D(t-t_1)}\, \exp\!\left[-\frac{(\mathbf{x}-\mathbf{x}_1)^2}{4D(t-t_1)}\right] \tag{2.112}$$

Edwards-Wilkinson (2d)

together with (2.106) to find (see problem 2.29)

$$C(\mathbf{x},t) = \frac{\Gamma}{4\pi D}\, E_1(\xi), \qquad \xi = \frac{\mathbf{x}^2}{8Dt}, \tag{2.113}$$

where $E_1(z)$ is the exponential integral.[20] Using the asymptotic behavior

$$E_1(z) = -\ln z - \gamma_E + z - \frac{z^2}{4} + \frac{z^3}{18} + \cdots$$

($\gamma_E \doteqdot 0.577215$ is the Euler constant), we see that

$$C(\mathbf{x},t) = \frac{\Gamma}{4\pi D}\left[\ln\left(\frac{8Dt}{\mathbf{x}^2}\right) - \gamma_E\right] \tag{2.114}$$

in the long-time limit.

Edwards-Wilkinson (2d)

The divergence of the width is resolved by noting that, in any physical situation, there is always a microscopic length a below which the assumption that noise is spatially uncorrelated is no longer valid. This cutoff is the natural shortest length beyond which the continuum description has no meaning. In lattice problems, a is the lattice spacing; in surface deposition problems, a is the atomic size. Mathematically, the factor $\delta(\mathbf{x} - \mathbf{x}')$ in the noise correlation function should be replaced by a function $f(\mathbf{x} - \mathbf{x}')$ that has the following properties:

- $f(\mathbf{0})$ is finite;
- $f(\mathbf{y})$ is a rapidly decaying function when $|\mathbf{y}| \gg a$;
- $\int d\mathbf{y}\, f(\mathbf{y}) = 1$, so that the magnitude of the noise is captured by parameter Γ.

The finite lower cutoff cures the divergence and leads to a width $w = \sqrt{(\Gamma/4\pi D)\ln(Dt/a^2)}$ that diverges logarithmically in the cutoff.

Edwards-Wilkinson (any d)

While the two-dimensional case is most natural in applications to surface evolution, a general lesson of statistical physics (and indeed of many other branches of physics) is to consider the behavior in general spatial dimensions. This generality can uncover regularities that may shed light on the behavior in the physically interesting dimension. The EW equation is tractable in any dimension, and the habit of considering general spatial dimensions is often useful. In the present case, the behavior of the two-point correlation function vividly demonstrates the importance of the spatial dimension:

$$C(\mathbf{x},t) = \frac{\Gamma}{4\pi D} \times \begin{cases} (8\pi Dt)^{1/2} E_{3/2}(\xi), & d=1, \\ E_1(\xi), & d=2, \\ (8\pi Dt)^{-1/2} E_{1/2}(\xi), & d=3. \end{cases} \tag{2.115}$$

In three dimensions, the two-point correlation function becomes time-independent in the long-time limit. From (2.115) we arrive at the following asymptotic behaviors:

$$w^2 = \Gamma \times \begin{cases} \sqrt{2t/\pi D}, & d=1, \\ (4\pi D)^{-1} \ln(Dt/a^2), & d=2, \\ (4\pi Da)^{-1}, & d=3. \end{cases} \tag{2.116}$$

Edwards-Wilkinson (d=1)

Interfacial fluctuations

$$w \sim t^{1/4}$$

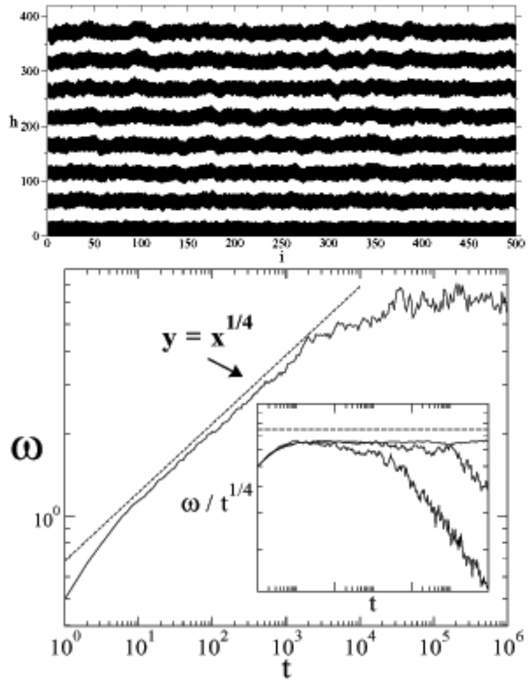


FIG. 1: In the top we show a typical profile for $\rho = 0.5$, $\kappa = 0.1$ and $L = 500$, where we change the color of the particles each 50 time steps and let the system evolve until $t = 750$. In the bottom, we have a log-log plot of the roughness ω as a function of time t, for $\rho = 0.5$, $\kappa = 0.1$ and $L = 200$, averaged over 200 samples. The traced line corresponds to the function $y = x^{1/4}$. In the inset we show the roughness divided by $t^{1/4}$ as a function of t, for $L = 10^2$, 10^3 and 10^4.

Edwards-Wilkinson (1d)

Although the width and more generally $C(x,t)$ remain non-stationary in one dimension, the height difference reaches a stationary limit. This feature can be appreciated by averaging the mean-square height. Using (2.115) we obtain

$$\begin{aligned}\langle [h(x,t) - h(0,t)]^2 \rangle &= 2[C(0,t) - C(x,t)] \\ &= \frac{\Gamma}{2\pi D}(8\pi D t)^{1/2}[E_{3/2}(0) - E_{3/2}(\xi)]. \end{aligned} \tag{2.117}$$

Writing

$$E_{3/2}(0) - E_{3/2}(\xi) = \int_1^\infty \frac{du}{u^{3/2}}\left[1 - e^{-u\xi}\right] \tag{2.118}$$

and differentiating with respect to ξ we find that the derivative approaches to $\sqrt{\pi/\xi}$ as $\xi \to 0$. Therefore the difference (2.118) behaves as $2\sqrt{\pi\xi}$ when $\xi \to 0$. Substituting this result into (2.117) gives

$$\langle [h(x,t) - h(0,t)]^2 \rangle = \frac{\Gamma}{D}|x| \quad \text{as} \quad t \to \infty. \tag{2.119}$$

This neat formula tells us that, in one dimension, the height $h(t,x)$ is (asymptotically) a random walk with respect to the spatial coordinate x.

Sir Sam Edwards

The EW equation gives a flavor of the vast subject of Langevin equations that are built upon partial differential equations. These equations are rarely solvable; those which are tend to be linear. One such solvable equation is the Mullins equation (see problem 2.31)

$$\frac{\partial h}{\partial t} = -\nu \nabla^4 h + \eta \,. \tag{2.120}$$

Similar (but often nonlinear) equations describe the phase-ordering kinetics at a positive temperature.[21]

Kardar-Parisi-Zhang

Similar to the EW equation, the Kardar–Parisi–Zhang (KPZ) equation has been proposed to mimic surface growth. This leads to a nonlinear Langevin equation that is much more challenging than the EW equation. Both the KPZ and EW equations assume that the surface is characterized by its height $h(\mathbf{x},t)$, and thereby $h(\mathbf{x},t)$ is considered as a single-valued function; physically, this means that there are no overhangs in the surface profile. Further, both equations are examples of a macroscopic description, where we are interested in spatial scales that greatly exceed the atomic scale. The chief distinction between the EW and KPZ equations is that the KPZ equation is nonlinear. The KPZ equation has the simple form[22]

$$\frac{\partial h}{\partial t} = D\nabla^2 h + \lambda(\nabla h)^2 + \eta, \tag{2.121}$$

yet the simplicity is illusory – the properties of this equation have been understood only in one spatial dimension.

Kardar-Parisi-Zhang

It is worth emphasizing that Eq. (2.121) is not a random example from a zoo of nonlinear Langevin equations – it is a unique specimen. Indeed, the *simplest* equation that is compatible with the symmetries of the problem is usually the most appropriate. From this perspective, notice that (2.121) is consistent with the following symmetries:

1. *Translation invariance along the growth direction*. This disallows the appearance of terms that involve the height function h explicitly; only derivatives of h can appear.
2. *Translation, inversion, and rotation symmetries in the basal plane* $\mathbf{x}$. These symmetries permit terms like $\nabla^2 h$, $\nabla^4 h$, even powers of gradient $(\nabla h)^2$, $(\nabla h)^4$, etc., but exclude odd powers of gradient (terms such as ∇h).

In principle, an equation of the form

$$\frac{\partial h}{\partial t} = D_1 \nabla^2 h + D_2 \nabla^4 h + \lambda_1 (\nabla h)^2 + \lambda_2 (\nabla h)^4 + \mu (\nabla^2 h)(\nabla h)^2 + \eta$$

is compatible with the above symmetries and it may even provide a better early-time description of a particular process than (2.121). Asymptotically, however, higher-order derivatives and higher-order terms are negligible, that is, $\nabla^2 h \gg \nabla^4 h$, $(\nabla h)^2 \gg (\nabla h)^4$, $(\nabla h)^2 \gg (\nabla^2 h)(\nabla h)^2$, and therefore we recover (2.121). If the process is additionally invariant under up/down symmetry, $h \to -h$, the nonlinear terms should vanish ($\lambda_1 = \lambda_2 = 0$) and we recover (2.105); if a symmetry additionally implies $D_1 = 0$, we obtain (2.120). These arguments explain the privileged role played by special equations, such as the EW equation, the Mullins equation, and the KPZ equation.

Note that the EW equation enjoys up/down symmetry, that is, symmetry under the transformation $h \longrightarrow -h$, which does not hold for the KPZ equation. This disparity suggests that if surface growth proceeds via deposition and evaporation and both processes balance each other, then the EW equation should provide a faithful description. If, on the other hand, one of the processes dominates, up/down symmetry is broken[23] and the EW equation (and more generally any Langevin equation that is linear in h) is inapplicable.

Kardar-Parisi-Zhang

Kardar-Parisi-Zhang

Let's try to extract as much as we can from the KPZ equation in the laziest way, that is, by dimensional analysis. For concreteness, we focus on the one-dimensional system. The width of the interface is a function of time and the parameters D, λ, Γ of the KPZ equation: $w = w(t, D, \lambda, \Gamma)$. Writing the dimensions of these variables, $[t] = T, [D] = L^2/T, [\lambda] = L/T$, and $[\Gamma] = L^3/T$, we see that two dimensionless complexes can be formed out of the four variables. Thus dimensional analysis gives

$$w = \sqrt{Dt}\, F(D^3 t/\Gamma^2, \Gamma\lambda/D^2)\,. \tag{2.122}$$

Recall that in the case of the EW equation we expressed the width in terms of one dimensionless variable $\kappa = D^3 t / \Gamma^2$ and then exploited the linearity of the EW equation to determine the width. For the nonlinear KPZ equation, the width is expressed as an unknown function of two variables and no further simplification appears feasible.

We now describe a useful trick that is surprisingly effective in the present context. The idea is to artificially *increase* the number of dimensions. In surface growth problems, there is an obvious difference between the lateral and vertical directions, and this suggests postulating different dimensions corresponding to these directions. We write $L = [x]$ for the transverse and $H = [h]$ for the vertical dimensions. Using (2.106) we get $[\Gamma] = [\eta]^2 LT$, while (2.121) gives $[\eta] = H/T$ and $[\lambda] = L^2/HT$. Therefore the dimensions of the relevant variables are

$$[t] = T, \quad [D] = \frac{L^2}{T}, \quad [\lambda] = \frac{L^2}{HT}, \quad [\Gamma] = \frac{H^2 L}{T}. \tag{2.123}$$

We want to find how the width w and the correlation length ℓ (which is the typical lateral separation between the points when their heights become uncorrelated) depend on the above four variables. We can form only one dimensionless variable $\Gamma^2\lambda^4 t/D^5$ out of the four variables (2.123). Taking into account that $[w] = H$ and $[\ell] = L$ and using dimensional analysis we obtain

$$w = \frac{D}{\lambda} F(\tau), \quad \ell = \sqrt{Dt}\, G(\tau), \quad \tau = \frac{\Gamma^2\lambda^4 t}{D^5}. \tag{2.124}$$

It is striking that a simple formal trick has brought such a huge simplification. One may wonder about the validity of the trick in the case of the EW equation. For the EW equation, we have three variables t, D, and Γ with independent dimensions, so dimensional analysis gives the full dependence on the parameters:

$$w \sim \Gamma^{1/2} (t/D)^{1/4}, \quad \ell \sim \sqrt{Dt}.$$

Thus for the EW equation, the application of this trick allows us to deduce the basic dependence of the width on physical parameters without invoking the linearity of the EW equation.

Unfortunately dimensional analysis alone for the KPZ equation cannot do better than give the scaling predictions of Eq. (2.124), which still involve unknown single-variable functions. It is also unknown how to proceed in two and higher dimensions. The one-dimensional case, however, is unique because a stationary solution to the Fokker–Planck equation for the probability distribution of h is known. The Fokker–Planck equation is the master equation for the probability distribution $\Pi[h]$. For the KPZ equation (and generally for the Fokker–Planck description of any partial differential equation), we must take into account that the probability distribution is a *functional* $\Pi[h(\mathbf{x})]$. Therefore partial derivatives with respect to h that appear in the Fokker–Planck equation should be replaced by functional derivatives.

In the case of the KPZ equation, the standard recipe of deriving the Fokker–Planck from the Langevin equation gives (see the discussion leading to Eq. (2.104))

$$\frac{\partial \Pi}{\partial t} = -\int d\mathbf{x}\, \frac{\delta}{\delta h}\left[\left(D\nabla^2 h + \lambda(\nabla h)^2\right)\Pi\right] + \Gamma \int d\mathbf{x}\, \frac{\delta^2 \Pi}{\delta h^2}\,. \tag{2.125}$$

In one dimension, this equation admits the stationary solution

$$\Pi = \exp\left[-\int dx\, \frac{D}{2\Gamma}\left(\frac{\partial h}{\partial x}\right)^2\right]. \tag{2.126}$$

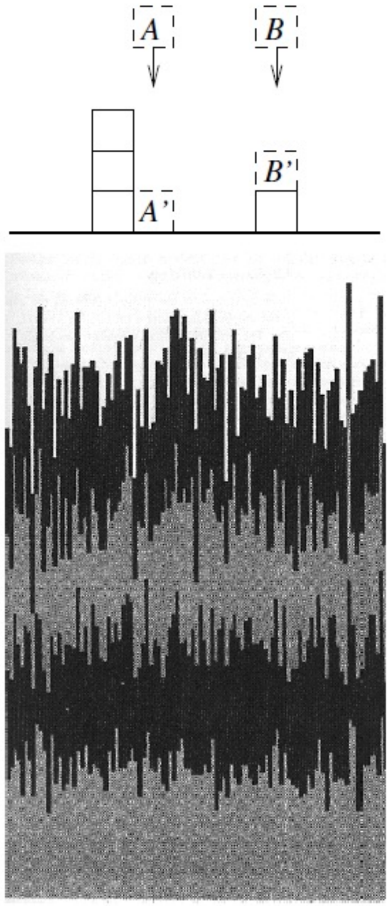
This form does *not* provide a solution in higher dimensions $d \geq 2$.

The simplest way to determine the growth laws in the one-dimensional KPZ equation is to notice that the parameters D and Γ appear only in the combination Γ/D in the long-time limit. Using this key property, we employ dimensional analysis[24] to seek the width and the correlation length as functions of t, λ, and Γ/D. These parameters have independent dimensions, and therefore we arrive at the full asymptotic dependence on model parameters:

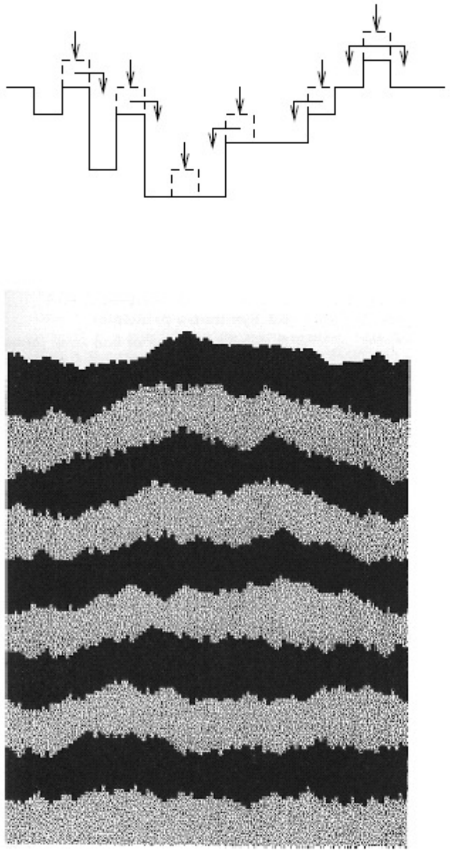
$$w \sim (\lambda t)^{1/3}(\Gamma/D)^{2/3}, \qquad \ell \sim (\lambda t)^{2/3}(\Gamma/D)^{1/3}. \tag{2.127}$$

These scaling behaviors are consistent with (2.124) when $F \sim \tau^{1/3}$ and $G \sim \tau^{1/6}$. The $t^{1/3}$ growth of the width is often called the KPZ growth and the 1/3 exponent is called the KPZ exponent.[25]

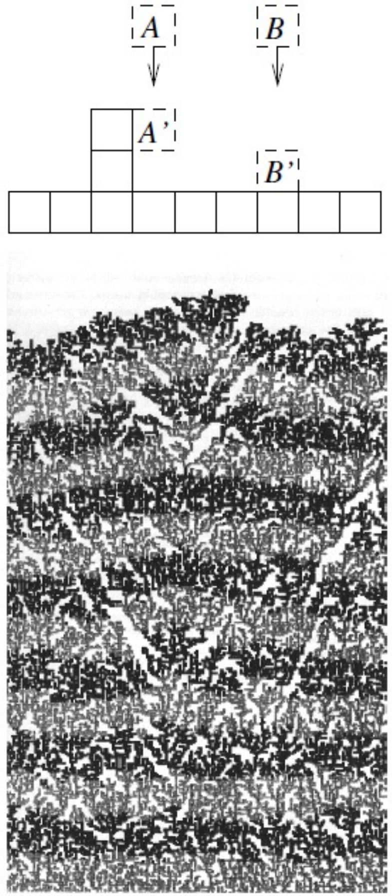
Random deposition

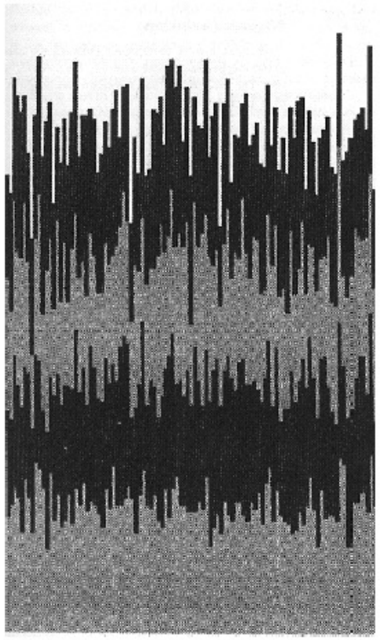
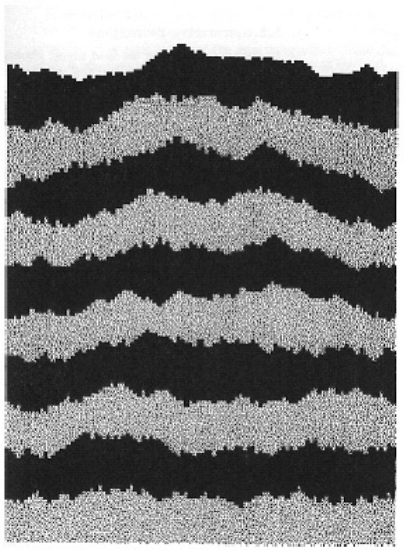
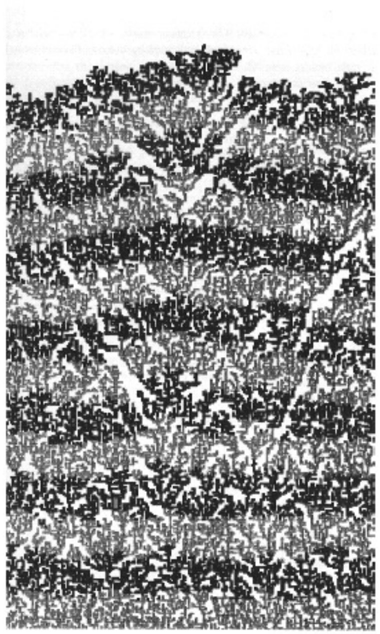


Random deposition with relaxation

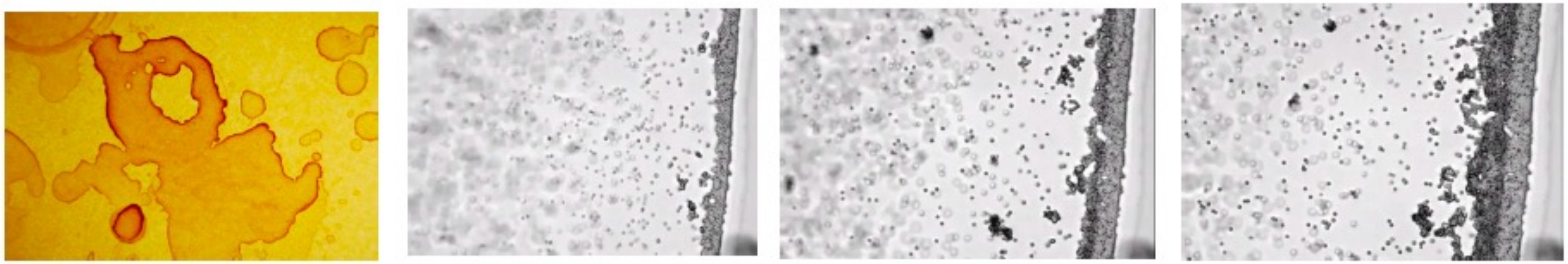


Ballistic deposition

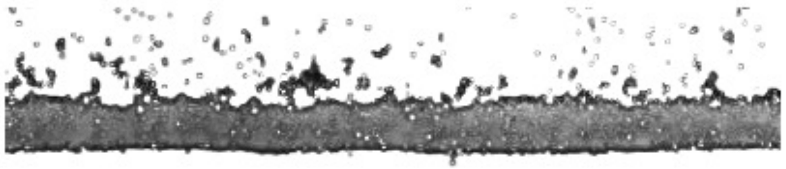


Classical CLT	Edwards-Wilkinson eq.	Kardar-Parisi-Zhang eq.
$\partial_t h = \eta(x,t)$	$\partial_t h = \nu\,\partial_x^2 h + \eta(x,t)$	$\partial_t h = \nu\,\partial_x^2 h + \lambda(\partial_x h)^2 + \eta$
$t^{\frac{1}{2}}$ fluctuations	$t^{\frac{1}{4}}$ fluctuations	$t^{\frac{1}{3}}$ fluctuations
		

Experimental example: coffee ring effect



Perfectly round particles:
$t^{1/2}$ fluctuations, CLT statistics



Slightly elongated particles:
$t^{1/3}$ fluctuations, KPZ statistics

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Interaction anisotropy and the KPZ to KPZQ transition in particle deposition at the edges of drying drops

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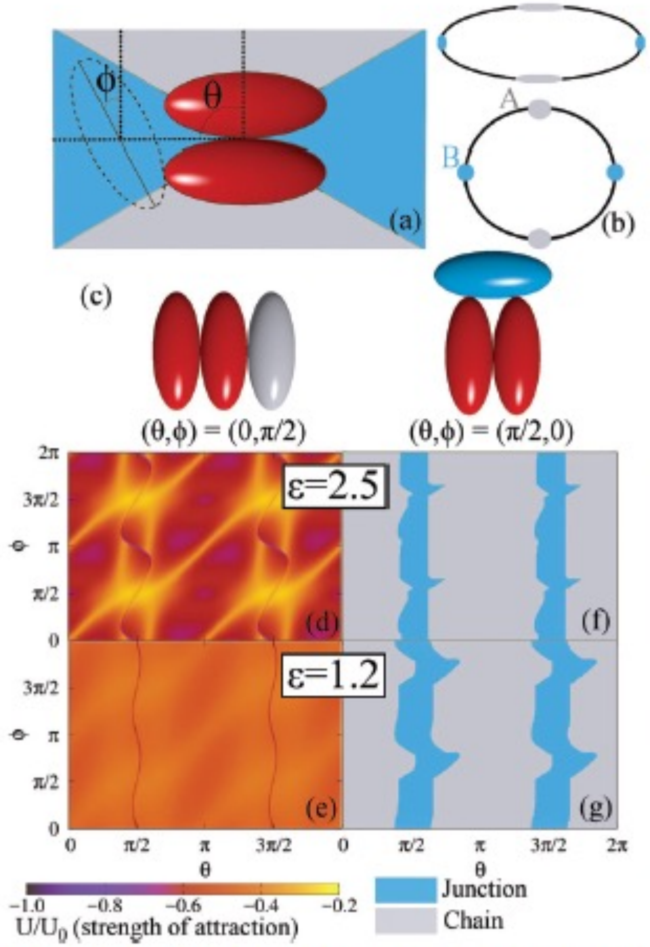
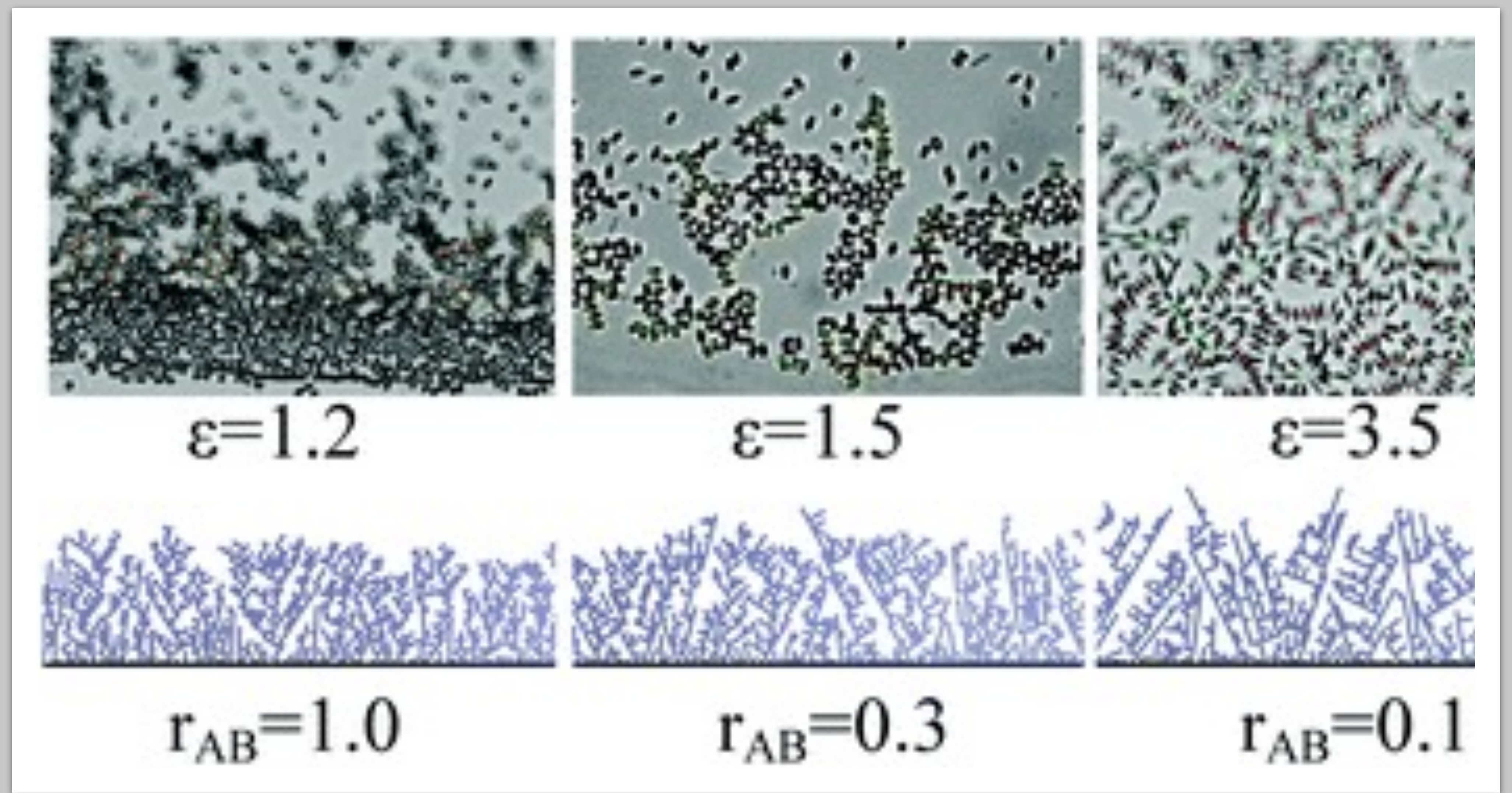
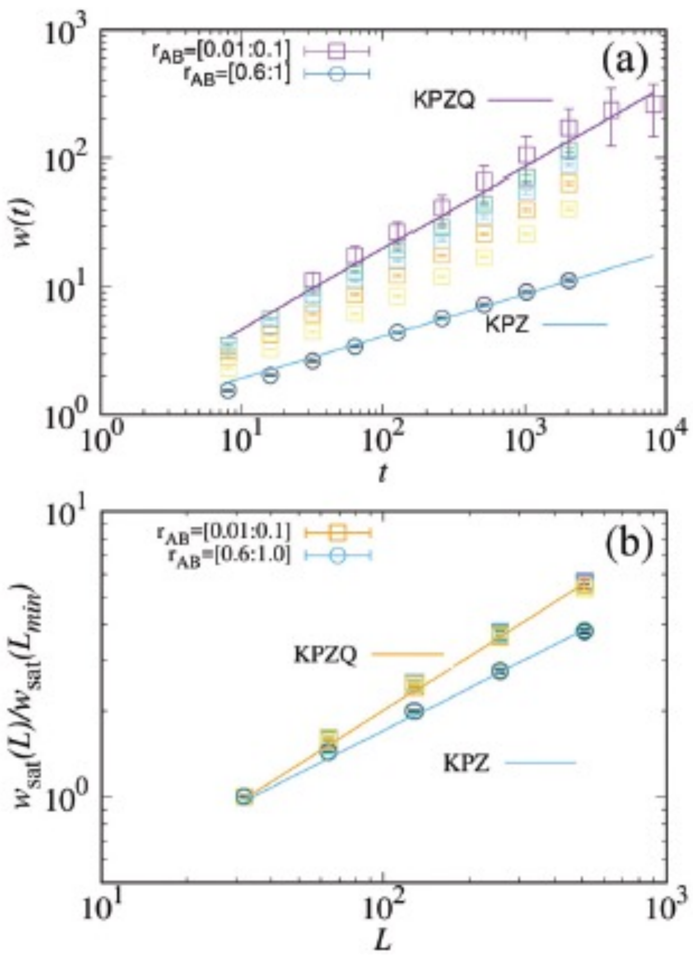
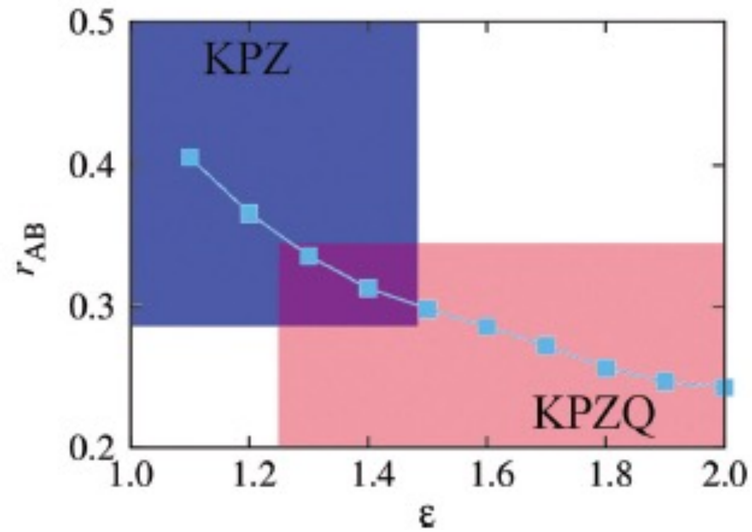
The deposition process at the edge of evaporating colloidal drops varies with the shape of suspended particles. Experiments with prolate ellipsoidal particles suggest that the spatiotemporal properties of the deposit depend strongly on particle aspect ratio. As the aspect ratio increases, the particles form less densely-packed deposits and the statistical behavior of the deposit interface crosses over from the Kardar–Parisi–Zhang (KPZ) universality class to another universality class which was suggested to be consistent with the KPZ plus quenched disorder. Here, we numerically study the effect of particle interaction anisotropy on deposit growth. In essence, we model the ellipsoids, at the interface, as disk-like




ε=1.2
ε=1.5
ε=3.5
r_{AB}=1.0
r_{AB}=0.3
r_{AB}=0.1

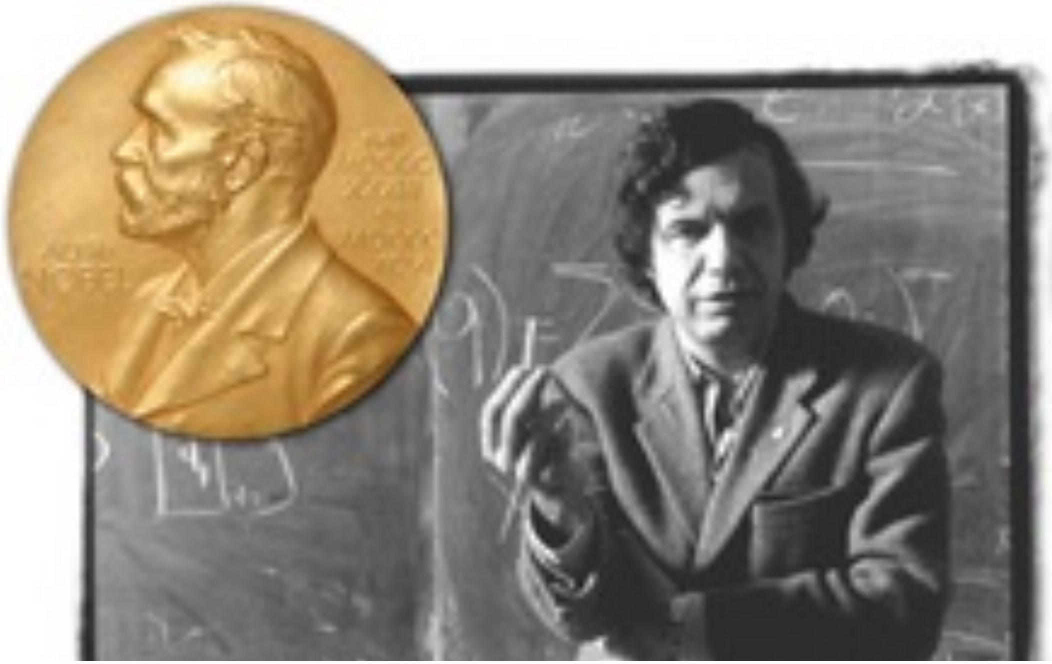


(a)
r_{AB}=[0.01:0.1]
r_{AB}=[0.6:1]
KPZQ
KPZ
$w(t)$
t
(b)
r_{AB}=[0.01:0.1]
r_{AB}=[0.6:1.0]
KPZQ
KPZ
$w_{sat}(L)/w_{sat}(L_{min})$
L



KPZ
KPZQ
r_{AB}
ε

Kardar and Parisi



Giorgio Parisi
awarded the
Nobel Prize in Physics 2021