

Microscopic Models of Macroscopic Behavior

Joel Lebowitz
Rutgers University

May 2013

1. Statistical Mechanics: An Overview
2. Phase Transitions
3. Derivation of Reaction-Diffusion Equations

The modern search for a quantitative microscopic theory of macroscopic phenomena dates to the middle of the nineteenth century. At that time the experiments of Joule and others made it clear that phenomena like boiling and freezing, heat conduction, diffusion, etc., have their origins in the dynamics of the atoms and molecules which are the constituents of matter.

It was also soon recognized that the large disparity in the spatial and temporal scales between the world of atoms and the world of macroscopic experience not only necessitated a statistical theory but also assured, in analogy to the law of large numbers in probability theory, that such a theory will give predictions precise enough to have the force of "law", as in Fourier's law or in the second law of thermodynamics

The twentieth century saw the development of the subject into a physically very successful and mathematically very beautiful theory of statistical mechanics of systems in thermal equilibrium. Statistical mechanics explains how cooperative behavior of the atoms gives rise to emergent phenomena such as phase transitions.

The development of a comparable theory for the more complex world of nonequilibrium phenomena, including in particular those occurring in biological systems, remains a challenge for the twenty-first century. This will require “cooperative behavior” between physicists, mathematicians, biologists,

Microstates: classical

Every bit of macroscopic matter is composed of an enormous number of quasi-autonomous units, the atoms or molecules. Treating these atoms as classical particles moving according to non-relativistic Hamiltonian equations the complete microscopic (or micro) state of an isolated classical system of N particles is specified at any time t by a point $X(t)$ in its phase space Γ ,

$$X = (\mathbf{r}_1, \mathbf{v}_1, \dots, \mathbf{r}_N, \mathbf{v}_N), \quad \mathbf{r}_i \in \mathbf{V} \subset \mathbb{R}^d, \quad \mathbf{v}_i \in \mathbb{R}^d,$$

with $X(t)$, $t \in \mathbb{R}$, given by the Hamiltonian evolution which takes place on an energy surface Γ_E .

Since the real world is quantum mechanical, such a classical description is clearly “not realistic”. That it works so well in many cases is (to me at least) very surprising. I will use it as a model of reality for this presentation.

Macrostates

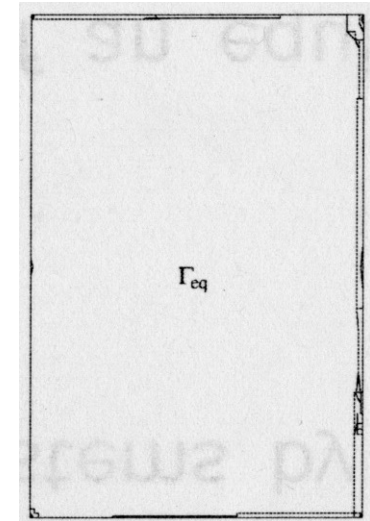
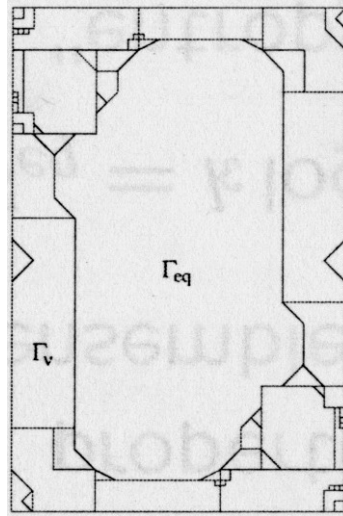
To describe the macroscopic state of a system of N atoms in a box V , say $N \gtrsim 10^{20}$, we make use of a much cruder description than that provided by the microstate X . We shall denote by M such a macroscopic description of a macrostate. As an example, we may divide V into K cells, where K is large but still $K \ll N$, and specify the number of particles, the momentum, and the amount of energy in each cell, with some tolerance.

This leads in suitable cases to a macroscopic description in terms of hydrodynamic density profiles, $\xi_X(\mathbf{x}) = (n(\mathbf{x}), \mathbf{u}(\mathbf{x}), e(\mathbf{x}))$, $\mathbf{x} \in V$. The time evolution of such profiles $\xi(\mathbf{x}, t) = \xi_{X(t)}(\mathbf{x})$ while coming from the dynamics of the microstates $X(t)$, take place on much coarser time and space scales. This permits the description of their evolution by autonomous equations, such as the Navier-Stokes and diffusion equation. The derivation (and solution) of such equations is one of the main subjects of classical non-equilibrium statistical mechanics.

Clearly, there are many microstates, X , in fact a continuum which correspond to the same macrostate, M . Let Γ_M be the region in the phase space Γ consisting of all microstates X corresponding to a given macrostate M , and denote by $|\Gamma_M|$ its (Liouville) volume.

The equilibrium macrostate M_{eq} of an isolated system with energy E is defined as that state for which $|\Gamma_{M_{eq}}| \sim |\Gamma_E|$, the volume of the whole “energy shell.” When $M(X)$ specifies a non-equilibrium state, $|\Gamma_{M(X)}|$ is much smaller. Thus, if a dilute gas contains N atoms in a volume V , then the ratio of $|\Gamma_{M_{eq}}|$ for the macrostate M_{eq} in which there are $\left(\frac{1}{2} \pm 10^{-10}\right) N$ particles in the left half of the box to $|\Gamma_M|$, corresponding to a macrostate M in which all the particles are in the left half, is of order 2^N . For any macroscopic value of N , this is far larger than the ratio of the volume of the known universe to the volume of one proton.

Pictorially



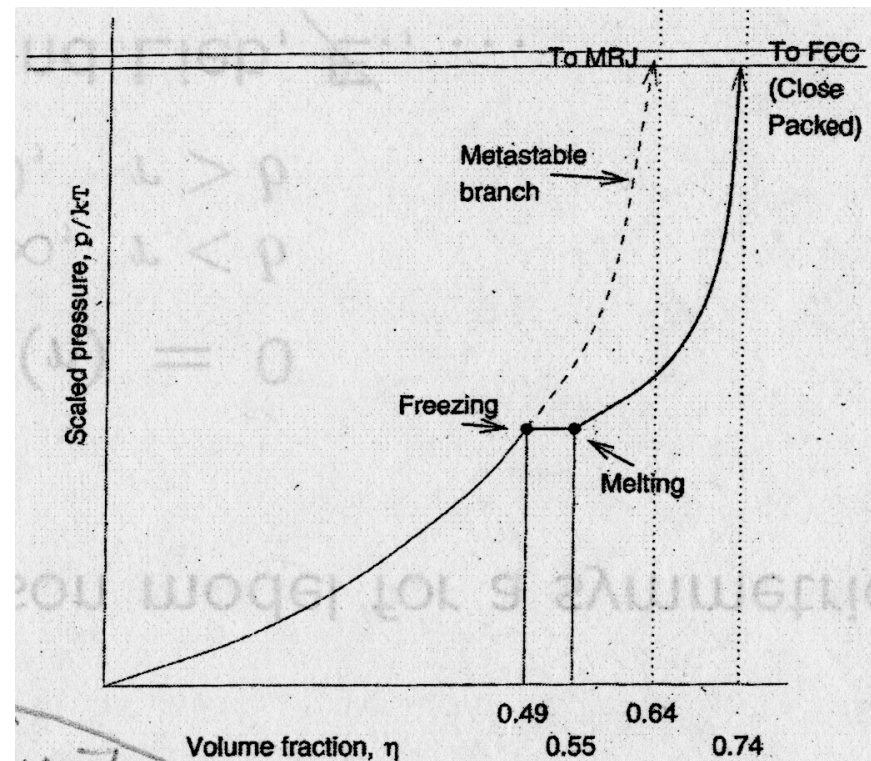
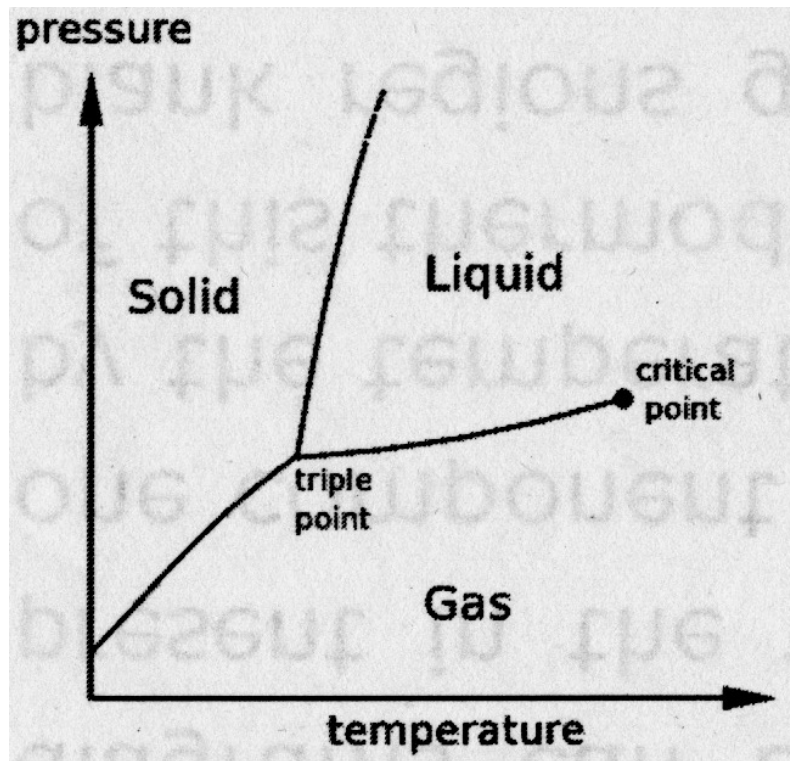
The second picture is slightly more faithful. Neither shows the topology or differences in relative sizes of the different Γ_M 's.

The fact that $|\Gamma_{\text{eq}}| \sim |\Gamma_E|$ explains why typical properties of equilibrium systems, i.e. those true for almost all $X \in \Gamma_{\text{eq}}$, are also typical for all $X \in \Gamma_E$ and can thus be obtained from the microcanonical ensemble. It also explains why isolated systems started in a nonequilibrium macro-state M_0 typically evolve into microstates M_t such that $|\Gamma_{M_t}|$ is increasing and end up in the equilibrium state.

Equating the entropy of a macroscopic system in the state M with $\log |\Gamma_M|$, Boltzmann gave a natural (and correct) explanation of the origin of the second law of thermodynamics: “the entropy of an isolated macroscopic system never decreases.”

Phase Transitions in Equilibrium Systems

Information about the equilibrium phases of a homogeneous macroscopic system is conveniently encoded in its phase diagram. Phase diagrams can be very complicated, but their essence is already present in the familiar, simplified two dimensional diagram for a one component system like water or argon. This has axes marked by the temperature T and pressure p , and gives the decomposition of this thermodynamic parameter space into different regions: the blank regions generally correspond to parameter values in which there is a unique pure phase — gas, liquid, or solid — while the lines between these regions represent values of the parameters at which two pure phases can coexist. At the triple point, the system can coexist in any of three pure phases.



(1) System with attractive interactions. (2) Hard sphere system.

The mathematically precise formulation of what is meant by coexistence of phases is a beautiful part of statistical mechanics. It is based on the observation that “boundary conditions” may influence the bulk state of a macroscopic system even when the volume V goes to infinity.

In general, a macroscopic system is said to *undergo* or *be at* a first-order phase transition when the temperature and pressure (or more generally, the temperature and chemical potentials) do not uniquely specify its homogeneous equilibrium state: the different boundary conditions will give rise to different pure phases. The different properties of the pure phases coexisting at such a transition manifest themselves as discontinuities in certain observables, e.g. a discontinuity in the density as a function of temperature at the boiling point.

How do we prove this?

“Done” for lattice systems, very challenging for continuum systems. Even more challenging are dynamical phase transitions. these can only be analyzed rigorously at the present time for lattice models with stochastic dynamics.

Stochastic dynamics for lattice systems

Let $x \in \Lambda \subset \mathbb{Z}^d$,

$$\begin{aligned}\eta(x) &= \{1, 0\}, \text{ occupied/empty,} \\ \sigma(x) &= 1 - 2\eta(x) = \pm 1.\end{aligned}$$

Glauber: $\sigma(x) \rightarrow -\sigma(x)$, rate $c(x; \underline{\sigma})$

$$\text{i.e, } \underline{\sigma} \rightarrow \underline{\sigma}^x, \quad \underline{\sigma}^x(y) = \begin{cases} \sigma(y) & , y \neq x \\ -\sigma(y) & , y = x \end{cases}$$

same as $\eta(x) \rightarrow 1 - \eta(x)$.

Kawasaki: spin exchange or hopping is given by:

$$\begin{aligned}\eta(x), \eta(y) &\rightarrow \eta(y), \eta(x), & \underline{\eta} &\rightarrow \underline{\eta}^{x,y} \\ \sigma(x), \sigma(y) &\rightarrow \sigma(y), \sigma(x), & \underline{\sigma} &\rightarrow \underline{\sigma}^{x,y}\end{aligned}$$

with rate $c(x, y; \underline{\sigma})$.

We can think of this as a particle “hopping” to an empty site with a rate $c(x, y; \underline{\eta})$

Master Equation

Stochastic dynamics give transition rates $K(\underline{\sigma}, \underline{\sigma}')$ for $\underline{\sigma}' \rightarrow \underline{\sigma}$. This leads to an equation for the probability $\mu(\underline{\sigma}, t)$,

$$\begin{aligned}\frac{\partial \mu(\underline{\sigma}, t)}{\partial t} &= \sum_{\underline{\sigma}'} [K(\underline{\sigma}, \underline{\sigma}') \mu(\underline{\sigma}', t) - K(\underline{\sigma}', \underline{\sigma}) \mu(\underline{\sigma}, t)] \\ &= \mathcal{L} \mu\end{aligned}$$

for Glauber

$$\mathcal{L}_G \mu = - \sum_x c(x; \underline{\sigma}) \mu(\underline{\sigma}) + \sum_x c(x; \underline{\sigma}^x) \mu(\underline{\sigma}^x)$$

for Kawasaki

$$\mathcal{L}_K \mu = - \sum_{x,y} c(x, y; \underline{\sigma}) \mu(\underline{\sigma}) + \sum_{x,y} c(x, y; \underline{\sigma}^{x,y}) \mu(\underline{\sigma}^{x,y})$$

Stationary state

$$\frac{\partial \tilde{\mu}}{\partial t} = 0 = \mathcal{L} \tilde{\mu}$$

Detailed balance of dynamics wrt $\tilde{\mu}$ iff :

$$K(\underline{\sigma}, \underline{\sigma}') \tilde{\mu}(\underline{\sigma}') = K(\underline{\sigma}', \underline{\sigma}) \tilde{\mu}(\underline{\sigma}).$$

Historically the Glauber and Kawasaki rates were chosen to satisfy detailed balance wrt some Gibbs measure, which describes the equilibrium state of the system.

$$\tilde{\mu} = \mu_{\text{eq}} = \exp[-\beta U(\underline{\sigma})]$$

Detailed balance then means,

$$\frac{c(x; \underline{\sigma})}{c(x; \underline{\sigma}^x)} = \exp\{-\beta[U(\underline{\sigma}^x) - U(\underline{\sigma})]\},$$

$$\frac{c(x, y; \underline{\sigma})}{c(x, y; \underline{\sigma}^{x,y})} = \exp\{-\beta[U(\underline{\sigma}^{x,y}) - U(\underline{\sigma})]\}.$$

Clearly, there are infinitely many rates satisfying detailed balance for same $\tilde{\mu}$. If one is only interested in the properties of the stationary equilibrium state, which are obtained as time averages over the evolution, one uses whichever rate is more convenient to implement.

Dynamic (Nonequilibrium) Models

In non-equilibrium situations the stochastic model is what describes the phenomena to be studied. the transition rates will then not generally satisfy detailed balance wrt the stationary state. Some examples of that are:

Basic Voter Model

A voter at site $x \in \mathbb{Z}^d$ with two options, $\sigma(x) = \pm 1$, randomly chooses a neighbor (at Poisson times) and adopts the neighbors politics

$$c_v(x; \underline{\sigma}) = 1 - \sigma(x) \frac{1}{2d} \sum_{y: |y-x|=1} \sigma(y)$$

What are the stationary states:

For finite domain $\Lambda \subset \mathbb{Z}^d$? For all of \mathbb{Z}^d ?

There are very many variations on this model.

Contact Process (epidemics)

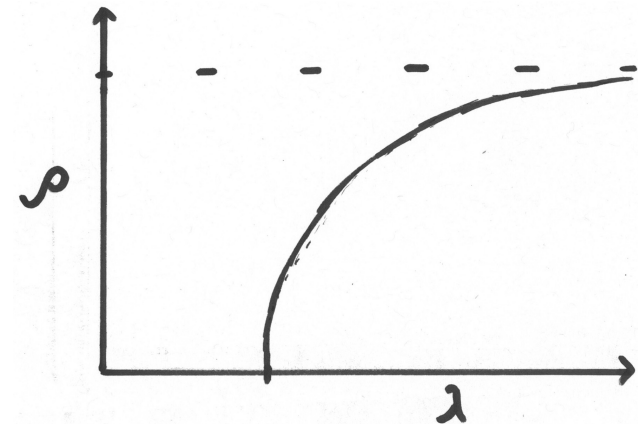
(SIS) Susceptible Infected Susceptible

An infected site ($\sigma(x) = 1$) gets cured at rate 1 and while infected it infects its neighbors at rate λ . This is like the voter model with the probability that someone in the wrong party (infected) spontaneously sees the light.

Stationary states ?

ρ = fraction of sites (probability of a given site being) infected. There is a phase transition at $\lambda_c = \lambda_c(d)$

Generalizations: SIRS, long range infection, etc.



“Hydrodynamical” Scaling

The formal way of going from a microscopic to a macroscopic description is via the rescaling of space and time. Let me illustrate this in the simplest example: the so called simple exclusion process (SEP).

Microscopic Evolution of SEP

In $d = 1$, with nearest neighbor jumps

$$\underline{\eta} = \{\eta(i)\} \quad \eta(i) = \{0, 1\}, \quad i \in \mathbb{Z}.$$

Particles attempt to jump to the neighboring site on right with rate 1 and to the left with rate $q \leq 1$: they succeed if the site on which they attempt to jump is empty, otherwise nothing happens.

For M particles on L sites, with periodic b.c., all $\binom{L}{M}$ configurations have equal weight in the stationary state.

For $q = 1$, SSEP, symmetric SEP, the dynamics satisfies *detailed balance* with respect to the stationary measure.

For $q < 1$, ASEP, asymmetric SEP, the dynamics doesn't satisfy detailed balance with respect to stationary measure.

For both SSAP and ASEP all stationary translation invariant measures on \mathbb{Z} are (superpositions of) Bernoulli or product measures with density $r \in [0, 1]$, $\text{prob}\{\eta(i) = 1\} = r$. Also true for \mathbb{Z}^d , $d > 1$, and more general jumps.

Hydrodynamical Scaling of SEP

$i \rightarrow x/\epsilon$, $s = t/\epsilon^\alpha$, x and t are macroscopic space and time scales, while i and s are the microscopic time variables.

Starting with initial configuration (or measure) on a system with L sites, whose density profile converges to $\rho_0(x)$, when $L \rightarrow \infty$,

$$\frac{1}{(b-a)L} \sum_{i=aL}^{bL} \eta(i) \rightarrow \int_a^b \rho_0(x) dx, \quad L = \epsilon^{-1}$$

The density profile $\rho(x, t)$ will then evolve in time according to a deterministic macroscopic equation:

$$\frac{\partial \rho(x, t)}{\partial t} = F(\{\rho\}), \quad \rho(x, 0) = \rho_0(x)$$

i.e.

$$\frac{1}{(b-a)L} \sum_{i=aL}^{bL} \eta(t/\epsilon^\alpha) \rightarrow \int_a^b \rho(x, t) dx.$$

Also true for \mathbb{Z}^d .

Euler Scaling, $\alpha = 1$

For $q < 1$ ASEP, $\alpha = 1$

$$\frac{\partial \rho(x, t)}{\partial t} + (1 - q) \frac{\partial}{\partial x} [\rho(1 - \rho)] = 0$$

Burger's Equation.

Diffusive Scaling, $\alpha = 2$

For $q = 1$, SSEP, “nothing” happens “on macroscopic scale” for times of order $\epsilon^{-1}t$. If, however, one waits for times of order $\epsilon^{-2}t$ one gets diffusive behavior

$$\frac{\partial \rho}{\partial t} = \frac{1}{2} \frac{\partial}{\partial x} \left[D(\rho) \frac{\partial \rho}{\partial x} \right]; \quad D = 1 \quad \text{for SSEP}$$

For $q = 1 - \lambda\epsilon$, WASEP, and $\alpha = 2$: one gets the viscous Burger's equation

$$\frac{\partial \rho(x, t)}{\partial t} + \lambda \frac{\partial}{\partial x} \rho(1 - \rho) = \frac{\partial^2 \rho}{\partial x^2}$$

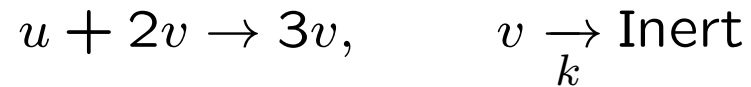
Reaction-Diffusion Equation (RDE)

Let me mention now briefly some old and current work on the derivation RDE from stochastic lattice models with both Glauber (reaction) and Kawasaki (diffusion) dynamics. An example of a RDE involving two species, with densities $u(x, t)$ and $v(x, t)$, is the well known (to some) Gray-Scott model

$$\frac{\partial u(x, t)}{\partial t} = D_u \nabla^2 u - uv^2 + F(1 - u)$$

$$\frac{\partial v(x, t)}{\partial t} = D_v \nabla^2 v + uv^2 - (F + k)v$$

where D_u and D_v are diffusion constants and the chemical reactions are



and F is some inflow/outflow rate to/from the system.

These equations which were derived to model an idealized form of some chemical reactions incorporate the “law of mass action”. One imagines that the “chemical tank” in which the reaction takes place is constantly stirred so that there are no correlations between the positions of the reacting molecules.

We model this on a lattice by having particles (of two types) hop very rapidly to neighboring empty sites as in a symmetric simple exclusion process (SSEP) and undergoing reactions, being created or annihilated, at rates which depend on their surrounding.

Formally the generator of the evolution (for a single species) in which $\eta(i) = 1, 0$ is given by

$$\mathcal{L} = \varepsilon^{-2} \mathcal{L}_K + \mathcal{L}_G.$$

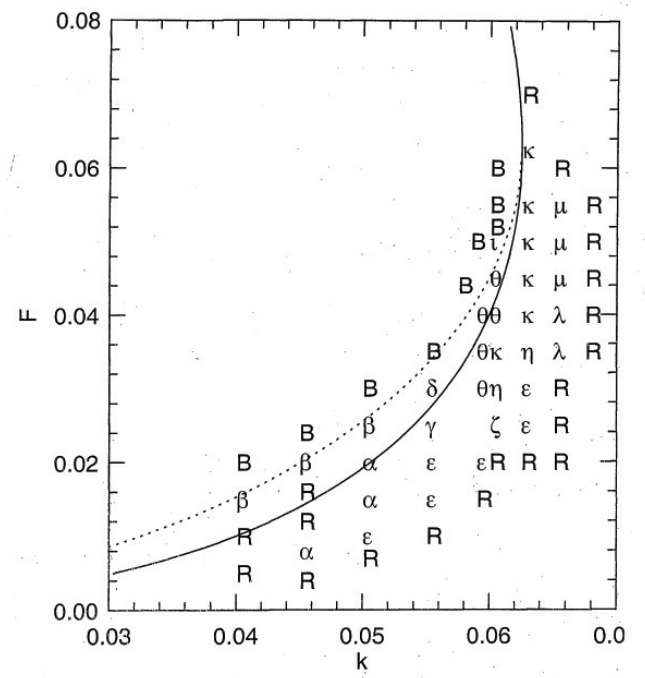
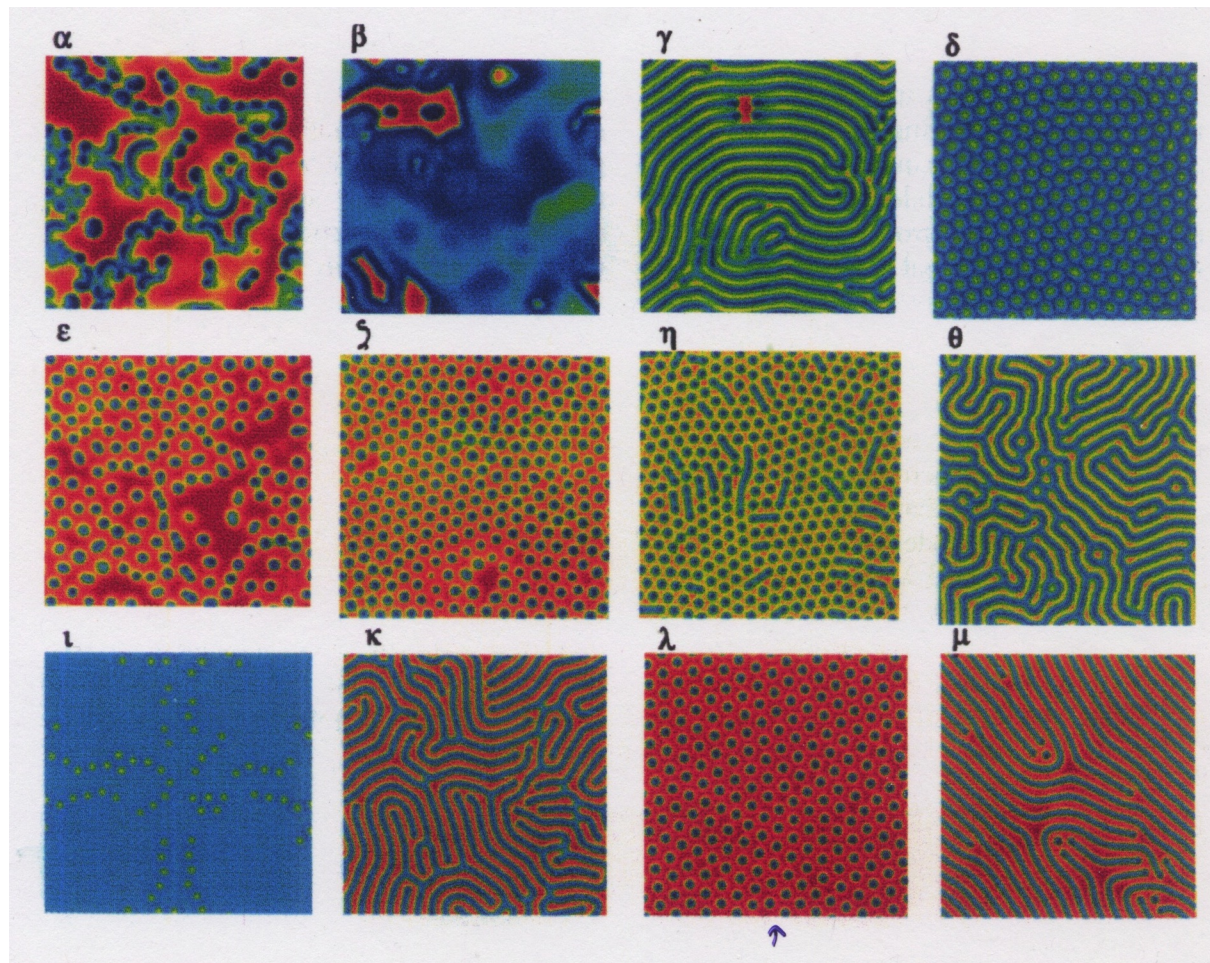
Then scaling space by ε , i.e. making the lattice spacing equal to ε , we rigorously obtain when $\varepsilon \rightarrow 0$, a RDE of the form

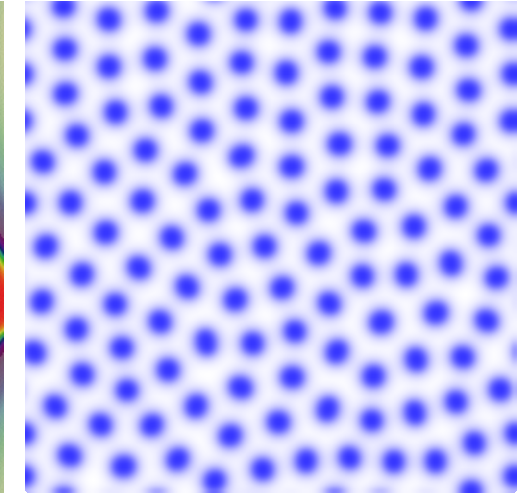
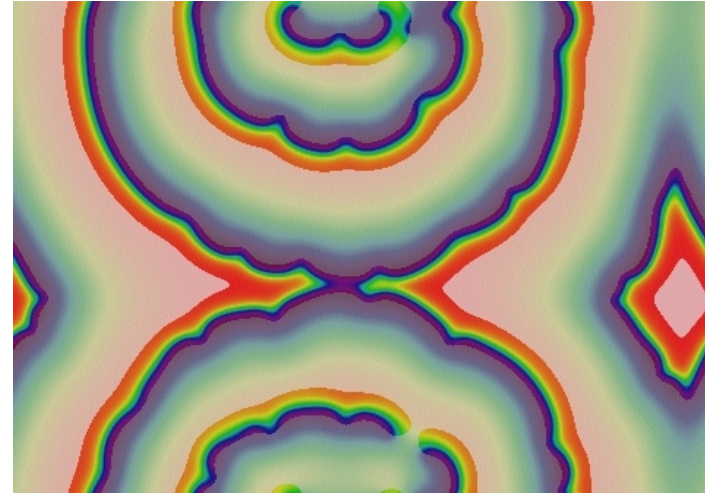
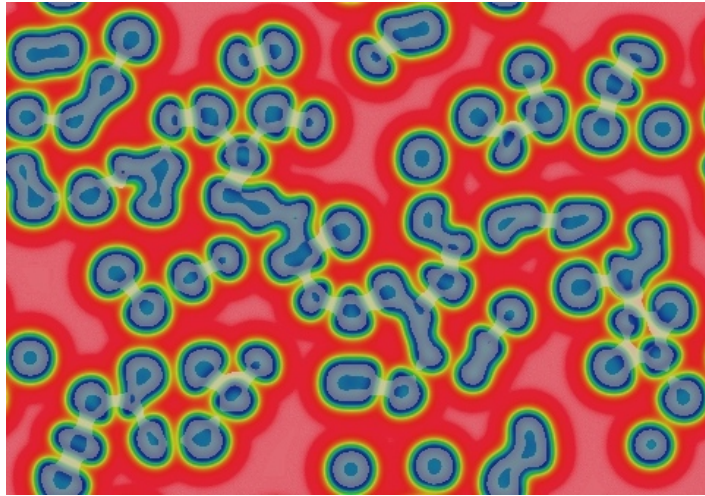
$$\frac{\partial \rho(x, t)}{\partial t} = D \nabla^2 \rho(x, t) + \mathcal{P}(\rho(x, t))$$

where $\mathcal{P}(\rho)$ is a polynomial in ρ .

The analysis is similar for modeling multispecies RDE such as the Gray-Scott one. There we permit at most one particle of each species per site.

Full disclosure: we have to twist a bit those equations to get them in our form but this does not seem to change the nature of the solutions, pictures of which I will now show you.





<http://mrob.com/pub/comp/xmorphia/>