

Lecture 12: Nonlinear Diffusion (October 19th, 2006)

In this lecture, concentration dependent drift and concentration dependent diffusion are described.

1. Concentration-dependent drift

A. A class of models

1) Traffic flow

In a traffic flow model, the governing equation can be derived from the mass conservation as:

$$\rho_t + (u(\rho)\rho)_x = D\rho_{xx}$$

where $\rho = \text{density of cars}$ and $u(\rho) = \text{velocity} = u_{\max}(1 - \rho/\rho_{\max})$. Furthermore, the wave speed, c , is defined as:

$$\rho_t + (u(\rho)\rho)_x = \rho_t + c(\rho)\rho_x$$

$$c(\rho) = \frac{d}{d\rho}(u(\rho)\rho) = \frac{dq}{d\rho}$$

Then, the diffusion coefficient can be correlated to a random walk model by:

$$D = \frac{M_2}{2\Delta t}$$

Two possible ways to use this diffusion coefficient for a step displacement in a random walk framework are:

a. $\Delta x = u(\tilde{\rho})\Delta t \pm \sqrt{2D\Delta t}$

b. $\Delta x = \left[u(\tilde{\rho}) - \frac{D\tilde{\rho}_x}{\tilde{\rho}} \right] \Delta t \equiv U\Delta t$

Since the material flux is defined as $F = \rho U$, the governing equation can be simply written as:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial F}{\partial x}$$

2) Burger's Equation in gas dynamics

When the wave speed $c = A + B\rho$, the governing equation can be written as follows:

$$c_t + cc_x = Dc_{xx}$$

which is called Burger's equation.

Graphical sketch for the solution of Burger's equation shows the evolution of shock structure as shown in Figure 1.

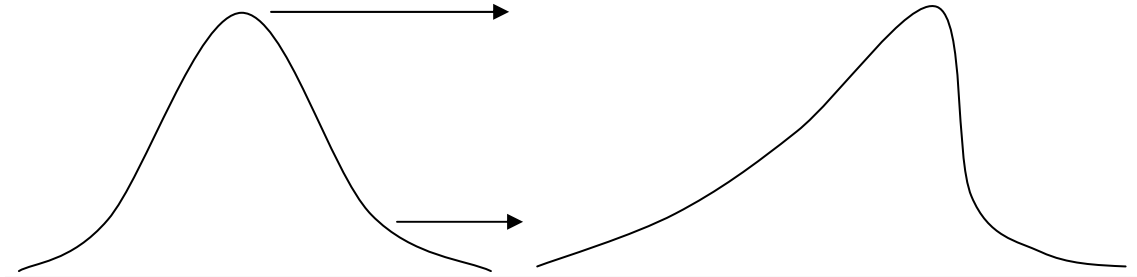


Figure 1. Universal shock structure described by Burger's equation

3) Kardar-Parisi-Zhang Equation in surface growth problem

When $c = -h_x$ ($h = \int_{x_0}^x c(x,t)dx$), we can write:

$$h_t = Dh_{xx} + \frac{1}{2}(h_x)^2 + F \quad \text{: KPZ equation}$$

Where F has white noise.

B. Shock solution

The Solution for Burger's equation can be obtained by defining a new variable, $\xi = x - vt$.

Then, the solution is:

$$c(x,t) = f(x - vt) = f(\xi)$$

$$f(\xi) = v + a \tanh\left(\frac{a\xi}{D}\right)$$

where $v = \frac{c_+ + c_-}{2}$ and $a = \frac{c_- - c_+}{2}$. The graphical representation of the solution is in Figure 2.

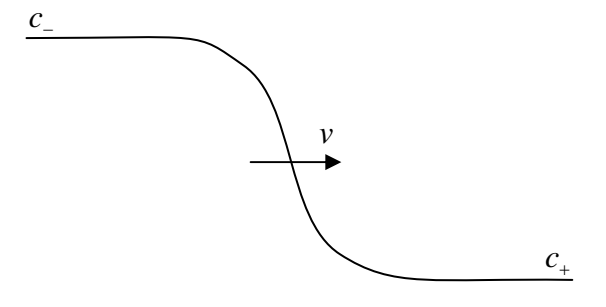


Figure 2. Solution for Burger's equation

C. General Solution

A general solution for KPZ equation can be found by Cole-Hopf transformation:

Step 1. $c = -h_x \rightarrow$ KPZ equation

Step 2. $\psi = e^{h/2D}$ or $h = 2D \log \psi$

Then,

$$h_t = \frac{2D\psi_t}{\psi}$$

$$h_x = \frac{2D\psi_x}{\psi}$$

$$h_{xx} = \frac{\psi\psi_{xx} - (\psi_x)^2}{\psi^2} 2D$$

$$\frac{2D\psi_t}{\psi} h_{xx} = D \frac{\psi\psi_{xx} - (\psi_x)^2}{\psi^2} 2D + \frac{1}{2} (2D)^2 \frac{(\psi_x)^2}{\psi^2} + F$$

$$\psi_t = D\psi_{xx} + \frac{F}{2D}\psi$$

which is a linear PDE and has a solution in the form of $\psi = e^{\frac{Ft}{2D}}\phi$, which is substituted for ψ in the previous equation to get:

$$\phi_t = D\phi_{xx}$$

General solution for this simple diffusion equation is:

$$\phi(x,t) = \phi_0 * G(x,t) = \int \phi_0(x-y)G(y,t)dy$$

where the initial condition is given by $\phi_0 = \phi(x,t=0)$ and the green function is:

$$G(x,t) = \frac{e^{-\frac{x^2}{4Dt}}}{\sqrt{4\pi Dt}}$$

Typical solutions for c , h , ψ , and ϕ at different times are shown in Figure 3.

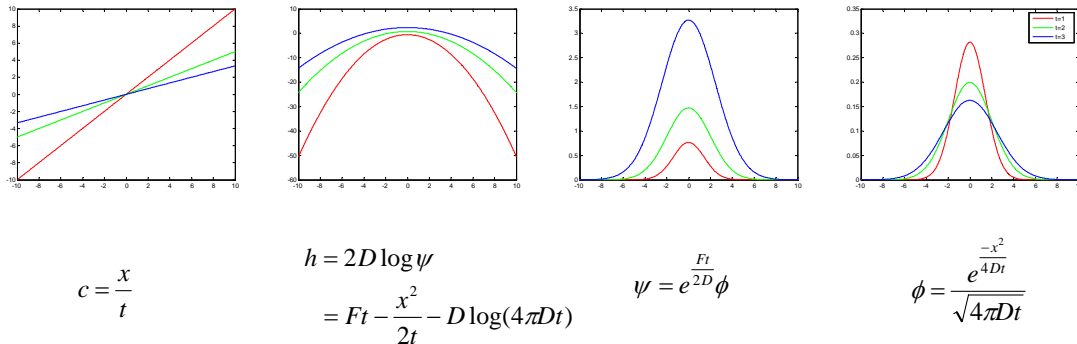


Figure 3. Solutions for c , h , ψ , and ϕ obtained by solving KPZ equation by Cole-Hopf

transformation

2. Concentration-dependent Diffusion

Concentration –dependent diffusion naturally arises in statistical mechanics for the approach to equilibrium. Free energy can be defined as:

$$H = U - TS, \quad H = H(\rho, \phi) = \int h(\rho, \phi) dx$$

where ρ : concentration

ϕ : external field (gravity, magnetic, electric, ...)

T : temperature

S : entropy

Equilibrium can be found by minimizing H , or by finding $\frac{\partial H}{\partial \rho} = 0$. And we can define chemical potential as:

$$\mu \equiv \frac{\delta H}{\delta \rho}$$

Near equilibrium, we can also write the mass conservation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot F = 0$$

where $F = -b\rho\nabla\mu(\rho)$

b : mobility

$u(\rho) = -b\nabla\mu(\rho)$

Then, the mass conservation equation is expressed as:

$$\frac{\partial \rho}{\partial t} = \nabla \cdot (D(\rho)\nabla\rho)$$

where $D(\rho) = \rho\mu'(\rho)b$.

One example of concentration-dependent diffusion is Li ion transport in rechargeable batteries. Figure 4 shows a schematic diagram of Li ion rechargeable batteries and the diffusion coefficient of Li ion as a function of its concentration. When the concentration is very low or high, the ions are not easy to move. However, it is much easier for the ions to diffuse when the cathode of the battery is filled with a certain concentration of Li ions and has a optimal configuration for Li ion diffusion

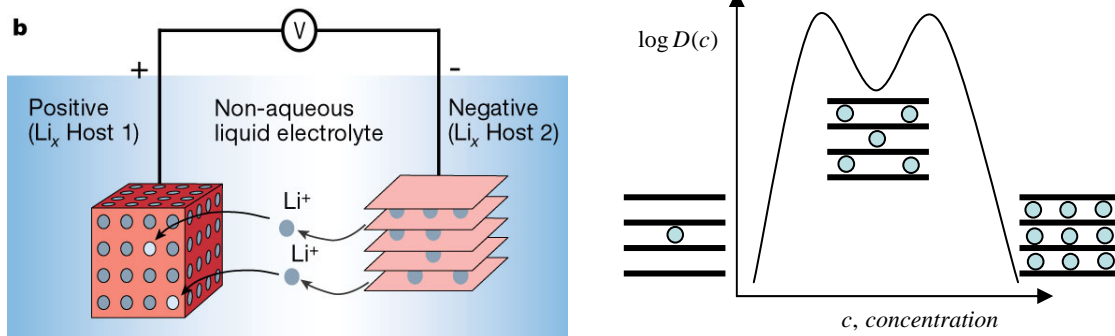


Figure 4. Schematic of Li ion rechargeable batteries (J.-M. Tarascon and M. Armand, *Nature*, **414**, 359-367 (2001)) and the diffusion coefficient of Li ion as a function of the concentration

Another example of concentration-dependent diffusion is diffusion of particles of finite size, which is called Steric effects as depicted in Figure 5. Steric effects arise from the fact that each atom within a molecule occupies a certain amount of space. If atoms are brought too close together, there is an associated cost in energy due to overlapping electron clouds (Pauli or Born repulsion), and this may affect the molecule's preferred shape (conformation) and reactivity.

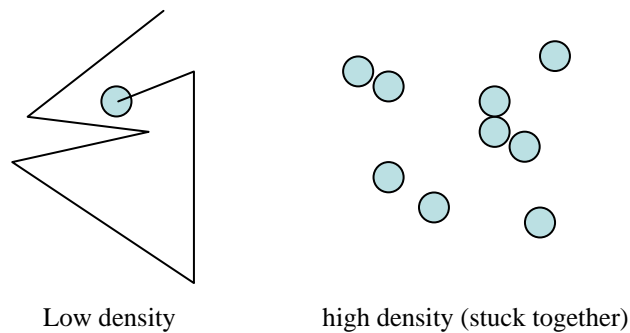


Figure 5. Diffusion of particles of finite size (Steric effects)

As aside it would be necessary to think about entropy from a statistical viewpoint. If N discrete states are occupied with probability, p_i , ($i = 1, 2, \dots, N$), then the entropy of the system is expressed as:

$$S = -k_B \sum_{i=1}^N p_i \log p_i$$

When $p_1 = 1$ and $p_i = 0$, ($i > 1$) which means the most ordered state, $S = 0$ (minimum entropy).

On the other hand, when $p_i = \frac{1}{N}$,

$$S = -k_B \log \frac{1}{N} = k_B \log N = S_{\max}.$$

Using the fact that ρa^3 is the probability of finding particle in a volume a^3 ,

$$S = \frac{-k}{a^3} \int [\rho a^3 \log(\rho a^3) + (1 - \rho a^3) \log(1 - \rho a^3)] dx$$

where the first term of the integrand is the entropy of particles and the second term is the entropy of solvent. Then, chemical potential can be expressed as:

$$\mu(\rho, \phi) = \frac{\delta H}{\delta \rho} = \frac{\partial h}{\partial \rho} = \phi + kT [\log(\rho a^3) + 1 - \log(1 - \rho a^3) - 1] = \phi + kT \log \frac{\rho a^3}{1 - \rho a^3}$$

Further more, the flux is

$$F = -b\rho \nabla \mu(\rho) = -b\rho \nabla \phi - bkT \nabla \rho + \frac{b\rho \nabla \rho}{1 - \rho a^3}$$

where the first term of the right hand side is drift due to force $(-\nabla \phi)$. From the second term, Einstein's relation, $D_0 = bkT$ can be found. The last term represents Steric effect. Finally the mass conservation leads to

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \left[b\rho \nabla \phi - bkT \frac{\nabla \rho}{1 - \rho a^3} \right]$$

where concentration-dependent diffusion coefficient can be defined as:

$$D(\rho) = \frac{D_0}{1 - \rho a^3}$$