Coarsening Phenomena

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Outline

- Ising Model
- Kinetic Ising Models
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- Conserved Order Parameter
  - The binary (AB) mixture or Lattice Gas
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Ising Model

The Ising Hamiltonian can be written as,

$$H = -J \sum_{\langle ij \rangle} S_i S_j - h \sum_{i=1} S_i \tag{1}$$

- The spins S_i can take values ± 1,
- $\langle ij \rangle$ implies nearest-neighbor interaction only,
- $J > 0$ is the strength of exchange interaction,
- h is the magnetic field.

In equilibrium at $T < T_c$ the system magnetises.
The system undergoes a 2nd order phase transition at T_c.

Nucleation

- First-order phase transitions usually occurs by nucleation and growth while second-order phase transitions proceed smoothly.
- Nucleation is the process whereby new phases appear at certain sites within a metastable phase
    - Homogeneous nucleation - occurs spontaneously and there is no preferred nucleation site but it requires superheating or supercooling of the medium
    - Heterogeneous nucleation - occurs at preferential sites such as container surfaces, impurities, grain boundaries, dislocations. The effective surface area is lower here, diminishing the free energy barrier and hence facilitating nucleation.
- Spinodal decomposition is more subtle than nucleation and occurs uniformly throughout.

Spinodal decomposition

- Spinodal decomposition is a mechanism by which a solution of two or more components can separate into distinct phases
- Mechanism of phase separation in SD differs from nucleation as it happens uniformly and throughout the system and not just at the nucleation sites.
- In spinodal region $\frac{\partial^2 F}{\partial c^2} < 0$, and hence there is no thermodynamic barrier to the growth of a new phase, i.e., the phase transformation is solely diffusion controlled.
- Phase separation usually occurs by nucleation and spinodal decomposition will not be observed. To observe SD, a very fast transition, a quench, is required to move from the stable to the spinodally unstable region.

Mean-Field Approximation

MF of Ising model due to Braggs-William replaces spin in the Hamiltonian by a spatially uniform magnetization, $\langle S \rangle = m$. The energy can thus be written as

$$E(m) \simeq -J \sum_{\langle ij \rangle} \langle S_i \rangle \langle S_j \rangle - h \sum_i \langle S_i \rangle = -\frac{NqJ}{2} m^2 - Nhm \qquad (2)$$

The entropy, S, can be calculated exactly

$$S(m) = k \ln \binom{N}{N_\uparrow} = k \ln \binom{N}{N(1+m)/2} \qquad (3)$$

$$(4)$$

$$= -Nk \left[\frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} - ln2 \right] \qquad (5)$$

where $N_\uparrow$ is number of up spins and $N = N_\uparrow + N_\downarrow$ is total number of sites in the lattice.

Braggs-William free energy, $f(m)$

The complete Braggs-William free energy is

$$\begin{aligned} f(T, m) &= (E - TS)/N \\ &= -\frac{NqJ}{2}m^2 - NkT\left[\frac{1+m}{2}\ln\frac{1+m}{2} + \frac{1-m}{2}\ln\frac{1-m}{2} - ln2\right] \end{aligned}$$

The expression can be expanded in the powers of m to obtain a simplified expression of free energy, f.

$$f = \frac{k(T - T_c)}{2}m^2 + \frac{kT}{12}m^4 - kTln2 + O(m^6) \tag{6}$$

where

$$T_c = \frac{qJ}{k}$$

for $T > T_c, f$ has a positive curvature at origin and negative curvature for $T < T_c$.

Also, by minimizing free energy at fixed *(T,h)* we can arrive at equilibrium value of order parameter:

$$m_0 = \tanh(\beta q J m_0 + \beta h) \tag{7}$$

For $h = 0$, we can again identify the MF critical temperature

$$T_c = \frac{qJ}{k} \tag{8}$$

Ginzburg-Landau theory

MF free energy of Ising model can be written in the form

$$f(m) = \frac{F(m)}{N} = \frac{1}{2}(kT - qJ)m^2 - hm + \frac{kT}{12}m^4 - kTln2 + O(m^6) \quad (9)$$

This form of free energy makes contact with the Landau functional

$$\mathcal{L} = \frac{a}{2}m^2 + \frac{u}{4}m^4 \quad (10)$$

Ginzburg-Landau functional considers spatial variation of order parameter as well,

$$\mathcal{G} = \frac{a}{2}m^2 + \frac{u}{4}m^4 + \frac{K}{2}(\nabla m)^2 \quad (11)$$

Kinetic Ising Models

- Ising model has no Hamiltonian given dynamics. For kinetics we assume that an associated heat bath generates spin flip ($S_i \to -S_i$).
- Purely dissipative and stochastic models are ofter referred to as Kinetic Ising models.
- Conserved and non-conserved cases can be describe as below:
  - The spin system. At the microscopic level, spin-flip Glauber model is used to describe the non-conserved kinetics of the paramagnetic to ferromagnetic transition.
  - The binary (AB) mixture or Lattice Gas. The spin-exchange Kawasaki model is used to describe the conserved kinetics of binary mixtures at the microscopic level.
- At the coarse-grained level the respective order parameters, $\phi(\vec{r}, t)$ are used to describe the dynamics.

Domain Growth with non-conserved kinetics

- At $t = 0$, a paramagnetic phase is quenched below the critical temperature T_c.
- The paramagnetic state is no longer the preferred equilibrium state.
- The far-from-equilibrium, homogenous, state evolves towards its new equilibrium state by separating in domains.
- These domains coarsen with time and are characterized by length scale $L(t)$.
- A finite system becomes ordered in either of two equivalent states as $t \to \infty$.
- The simplest kinetics Ising model for non-conserved scalar field $\phi(\vec{r})$ is the time dependent Ginzburg- Landau (TDGL) model.

- The equation of motion for ϕ can be written as:

$$\frac{\partial\phi}{\partial t} = -\Gamma\frac{\delta\mathcal{F}}{\delta\phi} + \theta(\vec{r}, t) \tag{12}$$

where $\frac{\delta\mathcal{F}}{\delta\phi}$ denotes functional derivative of free-energy functional

$$\mathcal{F}(\phi) = \int\left[F(\phi) + \frac{1}{2}K(\nabla\phi)^2\right] \tag{13}$$

Typical form of the free energy $F(\phi)$ is given in eqn 6.

The noise term has zero mean and has a white noise spectrum

$$\langle\theta(\vec{r}, t)\theta(\vec{r}^{\,'}, t^{'})\rangle = 2T\Gamma\delta(\vec{r} - \vec{r}^{\,'})\delta(t - t^{'}) \tag{14}$$

TDGL equation

- Using the ϕ^4-form of free energy (eqn 6) we arrive at the TDGL equation

$$\frac{\partial\phi}{\partial t} = \Gamma\left[a(T_c - T)\phi - b\phi^3 + k\nabla^2\phi\right] + \theta(\vec{r}, t) \qquad (15)$$

- It is evident that $\phi = 0$ is unstable for $T < T_c$ and stable for $T > T_c$.
- For $T < T_c$ we can write TDGL in terms of rescaled variables as:

$$\frac{\partial\phi}{\partial t} = \phi - \phi^3 + \nabla^2\phi \qquad (16)$$

Domain Growth

Lets linearize the rescaled TDGL equation about ϕ^*, i.e, $\phi = \phi^* + \delta\phi$. Plugging it back in TDGL equation and retaining only linear terms in $\delta\phi$, we get

$$\frac{\partial \delta\phi}{\partial t} = \phi^* + \delta\phi - \phi^{*3} - \phi^{*2}\delta\phi + \nabla^2\delta\phi \tag{17}$$

$$= (1 - 3\phi^{*2})\delta\phi + \nabla^2\delta\phi \tag{18}$$

Doing a Fourier transform we get

$$\frac{\partial \delta\phi}{\partial t} = (1 - 3\phi^{*2} - k^2)\delta\phi \tag{19}$$

So, for k=0, fluctuations along $\phi = 0$ will keep growing unless higher order terms stabilizes them.

Static Interfaces or Kinks

TDGL equation in dimensionless form is

$$\frac{\partial \phi}{\partial t} = \phi - \phi^3 + \nabla^2 \phi \tag{20}$$

Interface or kink can be obtained by steady state

$$\frac{d^2 \phi}{dz^2} = \phi - \phi^3 \tag{21}$$

The kink solution is

$$\phi_s(z) = tanh\left[\pm \frac{(z - z_0)}{\sqrt{2}}\right] \tag{22}$$

where z_0 is center of the kink. Thus $\phi = \pm 1$ except in the inter-facial region.

Allen-Cahn equation of motion for the interfaces

Writing TDGL equation in terms of inter-facial coordinates $(n, \vec{a})$

$$\nabla\phi = \left.\frac{\partial\phi}{\partial n}\right|_t \hat{n} \tag{23}$$

$$\nabla^2\phi = \left.\frac{\partial^2\phi}{\partial n^2}\right|_t \hat{n}\cdot\hat{n} + \left.\frac{\partial\phi}{\partial n}\right|_t \nabla\cdot\hat{n} \tag{24}$$

Finally, we use the identity

$$\left.\frac{\partial\phi}{\partial t}\right|_n \left.\frac{\partial t}{\partial n}\right|_\phi \left.\frac{\partial n}{\partial\phi}\right|_t = -1 \tag{25}$$

in the TDGL equation,

$$-\left.\frac{\partial n}{\partial t}\right|_\phi \left.\frac{\partial\phi}{\partial n}\right|_t = \phi - \phi^3 + \left.\frac{\partial^2\phi}{\partial n^2}\right|_t \hat{n}\cdot\hat{n} + \left.\frac{\partial\phi}{\partial n}\right|_t \nabla\cdot\hat{n} \tag{26}$$

$$\simeq \left.\frac{\partial\phi}{\partial n}\right|_t \nabla\cdot\hat{n} \tag{27}$$

Allen-Cahn equation of motion for the interfaces

We make the identification that $\left.\frac{\partial n}{\partial t}\right|_{\phi} = v(\vec{a})$ is normal inter-facial velocity which yields the Allen-Cahn equation

$$v(\vec{a}) = -\nabla \cdot \hat{n} = -K(\vec{a}) \tag{28}$$

where the curvature goes as $K \sim 1/L$ and $v \sim dL/dt$, which gives the diffusive growth law for non-conserved scalar fields

$$L(t) \sim t^{1/2} \tag{29}$$

Here, *L(t)* is the typical domain size.

The binary (AB) mixture or Lattice Gas

AB mixtures can be modeled using Ising model as follows

- Here $n_i^\alpha = 1$ or 0 is occupation number of species α.
- $n_i^A + n_i^B = 1$ for all the sites. The dynamics is conserved as numbers of A and B species are constant.
- So we can identify these numbers with S_i in the Ising Hamiltonian, i.e., $S_i = 2n_i^A - 1 = 1 - 2n_i^B$.
- And hence all the analysis of critical temperature goes through.
- Order parameter, $\phi = n^A(\vec{r}, t) - n^B(\vec{r}, t)$, is conserved as it satisfies the continuity equation.

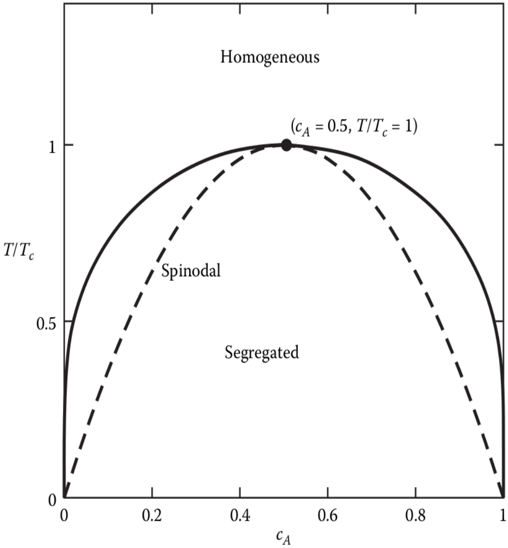

Figure: Phase diagram of a binary (AB) mixture.

Cahn-Hilliard equation

- Order parameter satisfies continuity equation

$$\frac{\partial \phi(\vec{r}, t)}{\partial t} = -\nabla \cdot \vec{J}(\vec{r}, t) \qquad \vec{J} \text{ is current} \tag{30}$$

$$\vec{J} = -D\nabla\mu(\vec{r}, t) \qquad \mu \text{ is chemical potential} \tag{31}$$

- The chemical potential is determined as

$$\mu(\vec{r}, t) = \frac{\delta \mathcal{F}}{\delta \phi} \tag{32}$$

- Plugging this back in continuity equation gives the Cahn-Hilliard (CH) equation for phase separation of binary mixture.

$$\frac{\partial \phi}{\partial t} = D\nabla^2 \left(\frac{\delta \mathcal{F}}{\delta \phi} \right) \tag{33}$$

Domain Growth

- For the ϕ^4-form of free energy (eqn 6), CH equation is

$$\frac{\partial \phi}{\partial t} = \nabla \cdot D \nabla [-a(T_c - T)\phi + b\phi^3 - k\nabla^2 \phi] \tag{34}$$

- Typical chemical potential of a domain of size L is $\mu \sim \frac{\sigma}{L}$.
- The concentration current is $D|\nabla \mu| \sim \frac{D\sigma}{L^2}$, where D is the diffusion constant.
- So domains grow as

$$\begin{aligned} \frac{dL}{dt} &\sim \frac{D\sigma}{L^2} \\ L(t) &\sim (D\sigma t)^{1/3} \end{aligned} \tag{35}$$

Summary

- A system evolves from its unstable or metastable state to its preferred equilibrium state as parameters like temperature, etc. are changed.
- Initially homogenous phase separates in phases rich in one of the constituents after quenching below T_c which is marked by emergence and growth of domains.
- The domain growth law depends critically on:
  - conservation law governing the coarsening.
  - nature of defects and dimensionality (d).
  - relevance of hydrodynamic flow fields
- The domain growth law for diffusive regime scales as:

$$L(t) \sim t^{\eta} \tag{36}$$

$\eta = 1/2$: for $d \geq 2$ and non-conserved order parameters.
$\eta = 1/3$: for $d \geq 2$ and conserved order parameters.

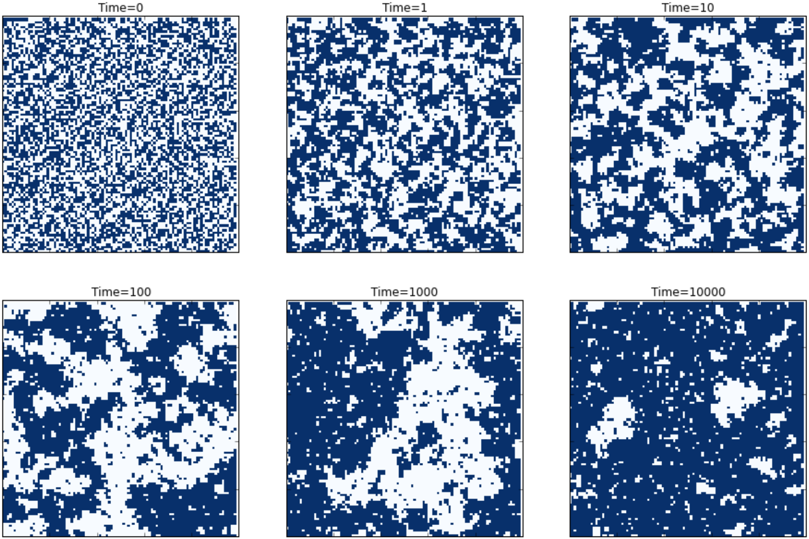

Figure: Domain growth in Monte carlo simulation of the Ising model.

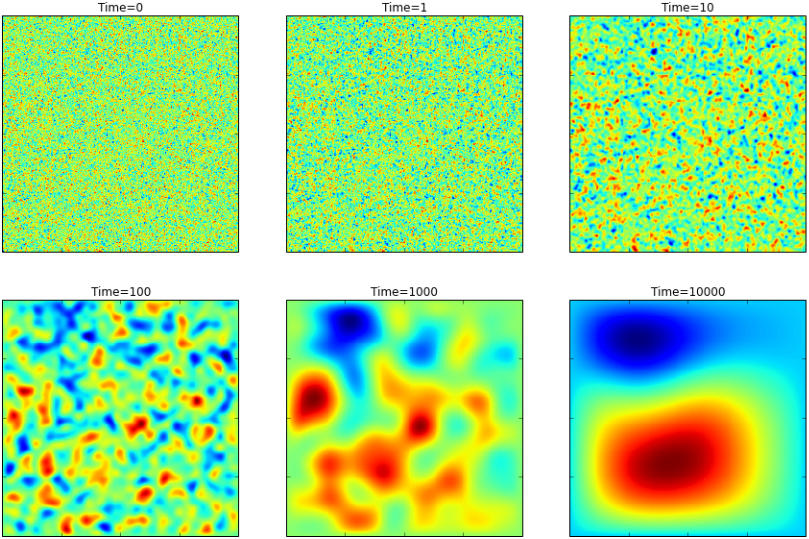

Figure: Domain growth in TDGL equation.

Thank You!

Appendix

The Spin-Flip Glauber Model

This model describes non-conserved kinetics since total magnetisation is time dependent on account of single-spin-flip processes.
The probablity of a state $\{S_i\}$ can be found using conditional probabilities of *ith* spin being in state $\{S_i\}$ at time t, given that it was in state $\{S_i^0\}$ at time t=*0*. Thus we can write the master equation:

$$\frac{dP(\{S_i\}, t)}{dt} = \sum_{j=1}^{N} W(...S_j, ...|... - S_j, ...)P(\{S_i^{'}\}, t) \\ - \sum_{j=1}^{N} W(... - S_j, ...|...S_j, ...)P(\{S_i\}, t) \tag{37}$$

The above equation is of the form *Gain-Loss*. Moreover the underlying stochastic process is *Markovian*.

The Spin-Flip Glauber Model

The *transition matrix* $W(\{S\}|\{S\}^{'})$ has to be modeled in a way such that ensemble approaches the equilibrium distribution, $P_{eq}(\{S_i\})$ as $t \rightarrow \infty$

$$P_{eq}(\{S_i\}) = \frac{exp[-\beta(H)]}{Z} \tag{38}$$

where, Z is the partition function defines as,

$$Z = \sum_{\{S_i\}} exp[-\beta(H)] \tag{39}$$

Also, detailed balance demands that

$$W(S_j^{'}|S_j)P(\{S_i\}) = W(S_i|S_j^{'})P(\{S_i^{'}\}) \tag{40}$$

The Spin-Flip Glauber Model

Lets choose Suzuki-Kubo form of transition matrix

$$W(S_j^{'}|S_j) = \frac{\lambda}{2}\{1 - tanh[\frac{-\beta\triangle H}{2}]\} \tag{41}$$

where λ^{-1} sets timescale of the non-equilibrium process. Using this we obtain

$$\frac{d\langle S\rangle}{dt} = -\langle S\rangle + tanh\left(\beta J\sum_{L_k}\langle S_{L_k}\rangle + \beta h\right) \tag{42}$$

The steady state solution will have,

$$\langle S\rangle^{eq} = tanh\left(\beta J\sum_{L_k}\langle S_{L_k}\rangle + \beta h\right) \tag{43}$$

These equations are often referred to as *mean-field dynamical models*.

The Spin-Exchange Kawasaki Model

In binary mixtures, the presence of atoms of A or B-type at lattice site is modeled by Ising model.
As order parameter is conserved we can only exchange the particles. Here Spin-Exchange Kawasaki Model is being considered to write the master equation

$$
\begin{aligned}
\frac{dP(\{S_i\},t)}{dt} &= \sum_{j=1}^{N}\sum_{K\epsilon L_j} W(...S_j,S_k,...|...S_k,S_j,...)P(\{S_i^{'}\},t) \\
&- \sum_{j=1}^{N}\sum_{K\epsilon L_j} W(...S_k,S_j,..|...S_j,S_k,...)P(\{S_i\},t)
\end{aligned}
\tag{44}
$$

where $K\epsilon L_j$ means nearest neighbors The above equation is of the form *Gain-Loss*. Moreover the underlying stochastic process is *Markovian*.

The Spin-Exchange Kawasaki Model

- We again choose the Suzuki-Kubo form for the transition probability.
- Finally, we arrive at what is called the *Cahn-Hilliard (CH)* equation.

$$2\lambda^{-1}\frac{\partial\phi}{\partial t} = -a^2\nabla^2\left(\frac{T_c}{T}-1\right)\phi - \frac{1}{3}\left(\frac{T_c}{T}\right)^3\phi^3 + \frac{T_c}{qT}a^2\nabla^2\phi + \ldots \tag{45}$$

  where a is the lattice spacing
- Growth law in the diffusive regime turns out to be:

$$L(t) \sim (t)^{1/3} \tag{46}$$