Phase Transition with Non-Thermodynamic States in Reversible Polymerization

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Talk, paper available from: http://cnls.lanl.gov/~ebn

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Aggregation-Fragmentation Processes

- **Aggregation**: merger of two small chains into a longer chain

$$[i] + [j] \xrightarrow{K_{ij}} [i+j]$$

Polymerization (Flory, Stockmeyer)

Random Graphs (Erdos, Renyi)

- **Fragmentation:** breakage of a large chain into to smaller chains

$$[i+j] \xrightarrow{F_{ij}} [i] + [j]$$

- Process is perfectly reversible when rates are non-zero

$$K_{ij} \neq 0 \qquad F_{ij} \neq 0$$

- Initial Condition: N monomers $c_k(t=0) = \delta_{k,0}$
- Goal: find the steady-state size distribution

The Master Equation

- Describes the evolution of the polymer size distribution

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} K_{ij}\, c_i\, c_j - c_k \sum_{j\geq 1} K_{kj}\, c_j + \sum_{j\geq 1} F_{kj}\, c_{j+k} - \frac{1}{2}\, c_k \sum_{i+j=k} F_{ij}$$

$$[i] + [j] \xrightarrow{K_{ij}} [i+j]$$

$$[i+j] \xrightarrow{F_{ij}} [i] + [j]$$

- Provides exact description when:
  - System is infinite (thermodynamic limit)
  - System is perfectly mixed (no spatial correlations)

Implicitly assumes size distribution is finite!

(number of chains of size k is proportional to N)

Equilibrium Steady-States

- Steady-state size distribution satisfies

$$0 = \frac{1}{2} \sum_{i+j=k} K_{ij}\, c_i\, c_j - c_k \sum_{j \geq 1} K_{kj}\, c_j + \sum_{j \geq 1} F_{kj}\, c_{j+k} - \frac{1}{2}\, c_k \sum_{i+j=k} F_{ij}$$

- Solve by equating aggregation and fragmentation fluxes
- Detailed balance condition

$$K_{ij}\, c_i\, c_j = F_{ij}\, c_{i+j}$$

- Fluxes between any two states of the system balance
- Example: constant rates yield an exponential distribution

$$K_{ij} = r, \qquad F_{ij} = 1 \qquad \Longrightarrow c_k \propto r^k$$

When do equilibrium solutions exist?

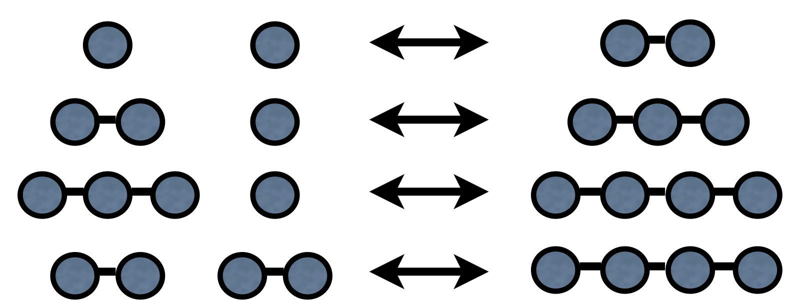
Detailed Balance Condition

- Detailed balance condition

$$K_{ij}\, c_i\, c_j = F_{ij}\, c_{i+j}$$

- For example, take k=1,2,3,4

$$K_{11}c_1^2 = F_{11}c_2$$
$$K_{12}c_1c_2 = F_{12}c_3$$
$$K_{13}c_1c_3 = F_{13}c_4$$
$$K_{22}c_2^2 = F_{22}c_4$$



- Solution exists only when rates satisfy the condition

$$\frac{K_{12}}{F_{12}}\frac{K_{13}}{F_{13}} = \frac{K_{11}}{F_{11}}\frac{K_{22}}{F_{22}}$$

- Detailed balance equation over-determined
- An infinite set of conditions on the rates

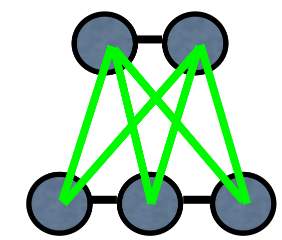
Generically, steady-state is nonequilibrium in nature

Product aggregation + constant fragmentation

- **Aggregation**: Constant reaction rate between any two monomers

random network (erdos-renyi)
gelation (flory-stockmayer)

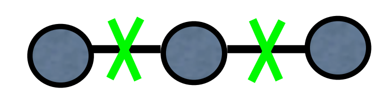
$$K_{ij} = ij$$



- **Fragmentation:** breakage of a large chain into to smaller chains

polymer degradation (ziff)

$$F_{ij} = \lambda$$



- Master equation

$$0 = \frac{1}{2}\sum_{i+j=k} ij\, c_i c_j - k\, c_k + \lambda \sum_{j>k}^{\infty} c_j - \frac{\lambda}{2}(k-1)c_k$$

- Detailed balance condition violated $\frac{K_{12}}{F_{12}}\frac{K_{13}}{F_{13}} \neq \frac{K_{11}}{F_{11}}\frac{K_{22}}{F_{22}}$

Nonequilibrium steady-state

Strong Fragmentation: Thermodynamic Phase

- Moments of the size distribution

$$M_n = \sum_{k=1}^{\infty} k^n c_k$$

$$0 = \frac{1}{2}\sum_{i+j=k} ij\, c_i c_j - k\, c_k + \lambda \sum_{j>k}^{\infty} c_j - \frac{\lambda}{2}(k-1)c_k$$

- Total density of clusters is finite when $\lambda > 1$

$$M_0 = 1 - \lambda^{-1}$$

$$\frac{1}{2} = \frac{\lambda}{2}(1 - M_0)$$

- Cluster size distribution is finite for all k

$$c_1 = \frac{\lambda - 1}{\lambda + 1} \qquad c_2 = \frac{(\lambda-1)(3\lambda+1)}{(\lambda+1)^2(3\lambda+4)}$$

- Large clusters are exponentially rare (from generating function)

$$c_k \sim k^{-5/2}\, e^{-\mathrm{const}\times k} \qquad k \to \infty$$

1. Finite density, number of clusters proportional to N
2. Many small clusters, few large clusters
3. Total density of clusters vanishes as $\lambda \to 1$???

Near critical behavior ($\lambda = 1 + \epsilon$)

- Perturbation analysis, small parameter $\epsilon = \lambda - 1$

$$c_k = \epsilon\, b_k \qquad \cancel{0 = \frac{1}{2}\sum_{i+j=k} ij\, c_i c_j} - k\, c_k + \lambda \sum_{j>k}^{\infty} c_j - \frac{\lambda}{2}(k-1)c_k$$

- Nonlinear convolution term irrelevant, linear equations

$$k\, b_k = \sum_{j=k+1}^{\infty} b_j - \frac{1}{2}(k-1)b_k$$

- Explicit linear recursion

$$\frac{b_{k+1}}{b_k} = \frac{k - \frac{1}{3}}{k + \frac{4}{3}} \qquad b_k \propto \frac{\Gamma(k - \frac{1}{3})}{\Gamma(k + \frac{4}{3})}$$

- Power-law size distribution over a diverging scale

$$c_k \sim \epsilon\, k^{-5/3} \qquad k \ll \epsilon^{-3}$$

1. Fewer small clusters, more large clusters
2. Nonlinear convolution term becomes irrelevant

Weak Fragmentation: Non-thermodynamic Phase

- Nonlinear convolution term is irrelevant, linear equations

$$k\,c_k = \lambda \sum_{j=1}^{k-1} c_j - \frac{\lambda}{2}\,(k-1)c_k \qquad \frac{c_{k+1}}{c_k} = \frac{k - \frac{\lambda}{2+\lambda}}{k + \frac{2(1+\lambda)}{2+\lambda}}$$

- Power-law size distribution, exponent varies

$$c_k \sim k^{-\beta} \qquad \beta = \frac{2+3\lambda}{2+\lambda} \qquad 1 < \beta < 5/3$$

- Mass conservation dictates system size dependence

$$c_k \sim N^{\beta-2} k^{-\beta} \qquad 1 = \sum_{k=1}^{N} k c_k$$

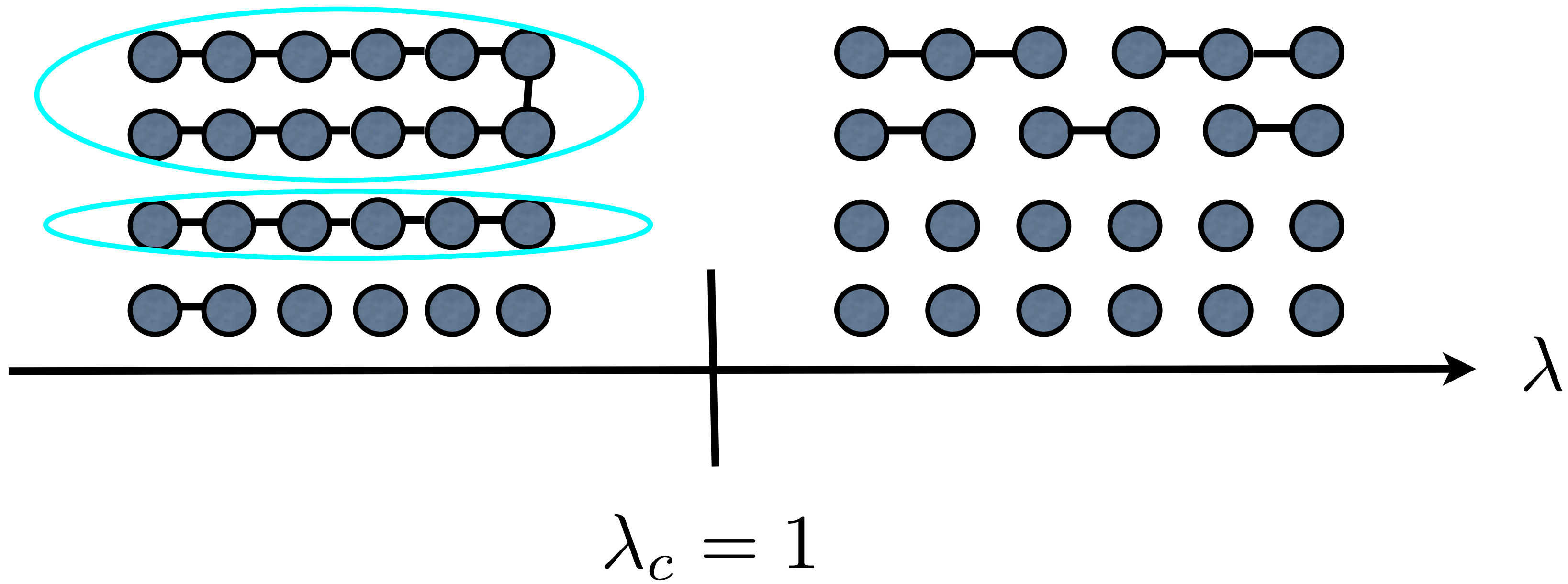
- Total number of clusters grows sub-linearly!

$$N_{\text{tot}} \sim N^{\gamma} \qquad \gamma = \frac{2\lambda}{2+\lambda} \qquad 0 < \gamma < 2/3$$

Nonthermodynamic state!

Number of clusters is not proportional to system size N

Microscopic vs Macroscopic Clusters



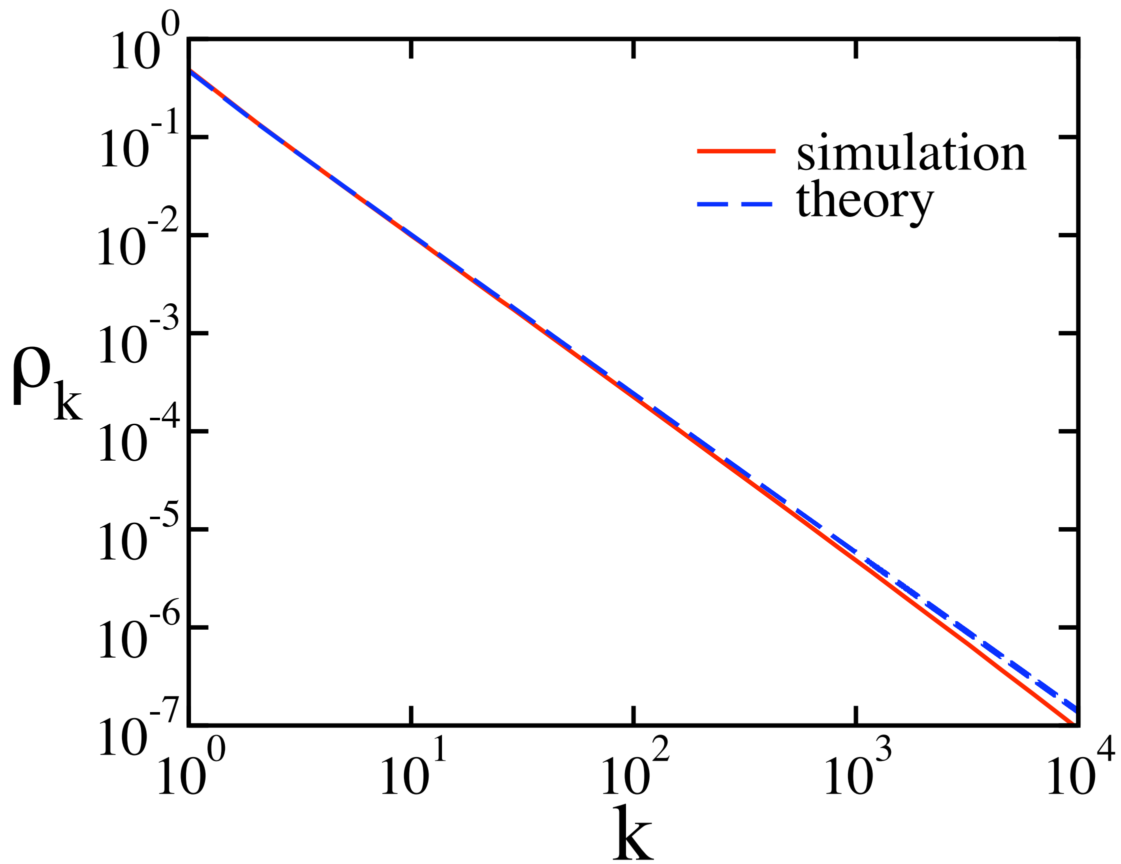
- Strong fragmentation: sizes on a finite scale
- Weak fragmentation: sizes on all scales
  - Macroscopic clusters ("gels") exist $\quad c_N \sim N^{-1}$
  - Macroscopic clusters contain finite fraction of mass

Master equations do not involve N!

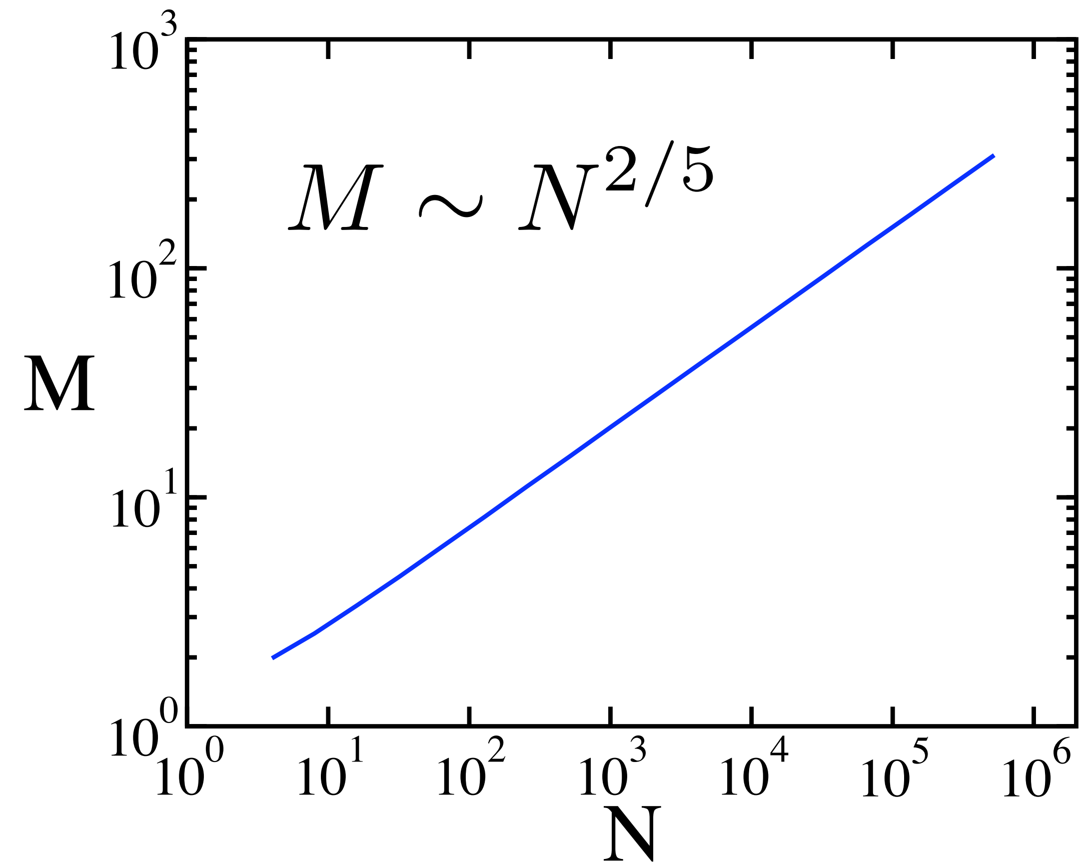
Monte Carlo Simulations

- Master equations "know nothing" about N
- Monte Carlo simulations involve N
- Sub-linear behavior causes slow convergence

power law size distribution



sub-linear number of clusters



Simulations confirm the theoretical predictions

Summary

- Nonequilibrium phase transition
- Strong fragmentation: thermodynamic phase
  - Number of clusters proportional to system size
  - Few large clusters (exponential tail)
- Weak fragmentation: nonthermodynamic phase
  - Number of clusters much smaller system size
  - Many large clusters (powerlaw tail)
  - Macroscopic clusters exist, contain finite fraction of mass
  - Giant fluctuations (macroscopic size)

Dramatic consequence of nonequilibrium dynamics