Phase Transition with Non-Thermodynamic States in Reversible Polymerization

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Aggregation-Fragmentation Processes

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

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

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

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

- Process is perfectly reversible when rates are non-zero

\[ K_{ij} \neq 0, \quad F_{ij} \neq 0 \]

- 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

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

- 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

\[ K_{ij} = r, \quad F_{ij} = 1 \implies c_k \propto r^k \]

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 \( k = 1, 2, 3, 4 \)

\[
\begin{align*}
K_{11} c_1^2 &= F_{11} c_2 \\
K_{12} c_1 c_2 &= F_{12} c_3 \\
K_{13} c_1 c_3 &= F_{13} c_4 \\
K_{22} c_2^2 &= F_{22} c_4
\end{align*}
\]

- 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 smaller chains
  - polymer degradation (ziff)
  \[ F_{ij} = \lambda \]

- **Master equation**
  \[ 0 = \frac{1}{2} \sum_{i+j=k} ij \, c_i c_j - k \, c_k + \lambda \sum_{j>k} c_j - \lambda \frac{\lambda}{2} (k - 1) c_k \]

- **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
  \[ M_n = \sum_{k=1}^{\infty} k^n c_k \]
  \[ 0 = \frac{1}{2} \sum_{i+j=k} ij c_i c_j - k c_k + \lambda \sum_{j>k} c_j - \frac{\lambda}{2} (k-1) c_k \]

- 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 \( k \)
  \[ c_1 = \frac{\lambda - 1}{\lambda + 1} \quad c_2 = \frac{(\lambda - 1)(3\lambda + 1)}{(\lambda + 1)^2(3\lambda + 4)} \]

- Large clusters are exponentially rare (from generating function)
  \[ c_k \sim k^{-5/2} e^{-\text{const} \times k} \quad k \to \infty \]

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 \(\epsilon = \lambda - 1\)
  \[ C_k = \epsilon b_k \]
  \[ 0 = \frac{1}{2} \sum_{i+j=k} c_i c_j - k c_k + \lambda \sum_{j>k} c_j - \frac{\lambda}{2} (k-1)c_k \]

- 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
  \[ \frac{b_{k+1}}{b_k} = \frac{k - \frac{1}{3}}{k + \frac{4}{3}} \]
  \[ b_k \propto \frac{\Gamma\left(k - \frac{1}{3}\right)}{\Gamma\left(k + \frac{4}{3}\right)} \]

- Power-law size distribution over a diverging scale
  \[ c_k \sim \epsilon k^{-5/3} \quad k \ll \epsilon^{-3} \]

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

- Power-law size distribution, exponent varies
  \[ c_k \sim k^{-\beta} \quad \beta = \frac{2 + 3\lambda}{2 + \lambda} \quad 1 < \beta < 5/3 \]

- Mass conservation dictates system size dependence
  \[ c_k \sim N^{\beta-2} k^{-\beta} \]
  \[ 1 = \sum_{k=1}^{N} k c_k \]

- Total number of clusters grows sub-linearly!
  \[ N_{\text{tot}} \sim N^{\gamma} \quad \gamma = \frac{2\lambda}{2 + \lambda} \quad 0 < \gamma < 2/3 \]

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
  - 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

Simulations confirm the theoretical predictions

**Power law size distribution**

\[ \rho_k = k^{-2}/\pi \]

**Sub-linear number of clusters**

\[ M \sim N^{2/5} \]
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