

Complementary Statistical Physics

Homework Set 2: Aggregation Kinetics

This problem set concerns irreversible aggregation, the Smoluchowski equations, the constant and product reaction kernels, and the onset of gelation. Show the essential steps of each derivation and explain the physical meaning of the results. For Problem 6, include both the AI-generated response and your independent verification.

Useful notation and relations

Let $c_k(t)$ denote the number concentration of clusters containing k monomers. For a symmetric aggregation kernel $K_{ij} = K_{ji}$, the Smoluchowski equations are

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

The moments of the cluster-mass distribution are

$$M_n(t) = \sum_{k \geq 1} k^n c_k(t), \quad N(t) = M_0(t), \quad M_1(t) = \sum_{k \geq 1} k c_k(t).$$

Masses are measured in monomer units. For monomer-only initial conditions $c_k(0) = \delta_{k1}$, the initial mass density is $M_1(0) = 1$. After gelation, the mass in finite clusters (the *sol*) is $M_1^{\text{sol}}(t) = 1 - g(t)$, where $g(t)$ is the gel mass fraction.

A. Smoluchowski equations and constant-kernel aggregation

Problem 1. Early stages of irreversible aggregation

Consider the Smoluchowski equations with a symmetric aggregation kernel K_{ij} and monomer-only initial conditions,

$$c_k(0) = \delta_{k1}.$$

- a) Determine the initial rates of monomer disappearance and dimer formation, $\dot{c}_1(0)$ and $\dot{c}_2(0)$.
- b) Obtain the first nonzero terms in the short-time expansions of $c_2(t)$ and $c_3(t)$.
- c) Evaluate these expressions for the constant kernel $K_{ij} = 2$ and the product kernel $K_{ij} = ij$. Compare the short-time production of dimers and trimers in the two models.

Problem 2. Constant kernel with a non-monomer initial distribution

Consider $K_{ij} = 2$, but assume an initial mixture of monomers and dimers,

$$c_1(0) = \frac{1}{2}, \quad c_2(0) = \frac{1}{4}, \quad c_k(0) = 0 \quad (k \geq 3).$$

- a) Calculate the initial number density $M_0(0)$, mass density $M_1(0)$, and second moment $M_2(0)$.

b) Derive and solve the evolution equations for these three moments.

c) Determine the time dependence of the mean cluster mass M_1/M_0 and the mass-weighted characteristic cluster mass M_2/M_1 .

d) Compare these results with monomer-only initial conditions having the same mass density.

Problem 3. Eliminating the loss terms

For the constant kernel $K_{ij} = 2$, introduce the concentration ratios (Krapivsky, Section 5.2)

$$\phi_k(t) = \frac{c_k(t)}{c_1(t)}.$$

a) Derive the equations satisfied by $\phi_k(t)$ and show that the common loss term disappears.

b) Introduce the new time variable

$$\tau = \int_0^t c_1(t') dt'$$

and derive the equations for $\phi_k(\tau)$.

c) For monomer-only initial conditions, solve these equations recursively and recover the exact distribution $c_k(t)$.

B. Product-kernel aggregation and gelation

Problem 4. Moments and the approach to gelation

Consider the product kernel $K_{ij} = ij$ with monomer-only initial conditions.

a) Derive the evolution equations for $M_0(t)$, $M_2(t)$, and $M_3(t)$ before gelation.

b) Solve the moment equations and show that

$$M_2(t) = \frac{1}{1-t}, \quad M_3(t) = \frac{1}{(1-t)^3}, \quad t < 1.$$

c) Determine the mean cluster mass M_1/M_0 and the mass-weighted characteristic cluster mass M_2/M_1 as $t \rightarrow 1^-$.

d) Explain why the divergence of the second moment does not imply a divergence of the mean cluster mass.

Problem 5. Critical distribution and the cutoff mass

For the product kernel, the exact finite-cluster distribution (for monomer-only initial conditions) is

$$c_k(t) = \frac{k^{k-2}}{k!} t^{k-1} e^{-kt}.$$

- a) Use Stirling's approximation to obtain the large- k behaviour at the gelation time $t_g = 1$.
- b) Determine which of the moments M_0 , M_1 , and M_2 remain finite at t_g .
- c) For $t < 1$, show that the large- k distribution has an exponential cutoff of the form

$$c_k(t) \propto k^{-5/2} \exp[-k/k_c(t)].$$

Determine $k_c(t)$ and its divergence as $t \rightarrow 1^-$.

C. AI-assisted theoretical investigation

Problem 6. Can AI correctly describe gelation?

Consider irreversible aggregation with the product kernel $K_{ij} = ij$ and monomer-only initial conditions. Before gelation, the cluster number density satisfies

$$N(t) = 1 - \frac{t}{2}, \quad t < 1.$$

- a) **AI-generated derivation.** Ask an AI assistant to derive the evolution equation for $N(t)$ and investigate whether the expression above remains valid after the gelation time $t_g = 1$. Request a clear explanation of the assumptions used.
- b) **Critical examination.** Independently examine the AI's derivation. Does conservation of total mass imply that the mass contained in finite clusters remains equal to one after gelation? Identify any unjustified assumptions and explain their consequences.
- c) **Correct post-gel description.** Using the gel mass fraction $g(t)$, derive the evolution equation for the number density of finite clusters after gelation. Compare it with the pre-gel equation and explain the physical origin of the difference.

Submission: Include the AI-generated response, your independently verified calculations, and a brief assessment of the AI's reasoning.