

## 1.2 Gelation (Phase) Transition in Coagulating Systems

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### Soft gels and gelation: Macroscopic and microscopic perspective

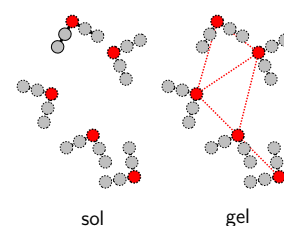
Gels are versatile materials that combine physical properties of liquids and solids. Typical examples for gels include gelatin used in food applications, gels and emulsions for medical products, and hydrogels in contact lenses. Hydrogels also play a crucial role in biomedical applications, particularly in tissue engineering, for their biocompatibility and ability to mimic the extracellular matrix, which provides a scaffold and mechanical support for maintaining the structure and function of living tissues. Gels consist of random networks of crosslinked particles, often formed by polymers that connect through entanglements or chemical bonds. These bonds can be created or broken through dynamic processes, allowing the network to adapt and evolve over time. Here, particles are broadly defined to include polymers or clusters of crosslinked polymers.

The transition of a liquid-like suspension of particles, known as a *sol*, into a solid-like structure, called a *gel*, occurs through a process known as *gelation*, as sketched in Figure 1. This process involves the formation of crosslinks between particles, creating a stable and flexible network, i.e. a percolating, dynamic structure with distinctive macroscopic viscoelastic properties. Gels exist in a complex environment shaped by chemical composition, ions and charges, temperature, pH, pressure, and external forces such as mechanical stress or electric fields, all of which influence gelation.

These chemical and physical properties call for a complex mathematical framework for predicting their behavior. Understanding gels and the process of gelation requires a dual approach: examining the reversible and irreversible bonding processes that lead to the creation of polymer (particle) networks, and analyzing the macroscopic transition in viscoelastic properties due to these bonding processes.

Research in the WIAS Main Application Areas Materials Modeling and Flow and Transport focuses on gels as macroscopic systems with distinct mechano-chemical properties. In contrast, the research topic Coagulation emphasizes the microscopic properties of particle systems and the study of their gelation processes via the concept of coagulation. Research at WIAS aims to bridge these approaches by combining the microscopic stochastic particle interpretation with the macroscopic continuum representation of materials, working towards a unified understanding of gelation.

The nature of gelation, whether it constitutes a thermodynamic process driven by energy and entropy or a kinetic process governed by crosslinking rates, remains a subject of debate and connects thermodynamic continuum models with particle-based coagulation models. While thermodynamic approaches emphasize free energy landscapes and kinetic models focus on bond and cluster formation dynamics, combining these viewpoints promises deeper insights into the interplay between the microscopic and the macroscopic perspective.



**Fig. 1:** Sketch shows gelation transition from uncrosslinked polymers (*sol* phase) on the left to crosslinked polymers (*gel* phase) on the right due to the formation of bonds (dotted lines) creating an elastic polymer network

### Continuum approaches for soft visco- and poroelastic gels

Continuum models for soft gels typically involve systems of partial differential equations (PDEs) to describe strongly coupled viscoelastic and poroelastic phenomena. In particular, their softness and swelling, caused by solvents in polymer networks or water in hydrogels, are typically modeled using nonlinear PDEs. In the presence of mechano-chemical effects, such systems are characterized by a free energy

$$\mathcal{F} = \int_{\Omega} W(F_e, \varphi, \nabla \varphi) dx,$$

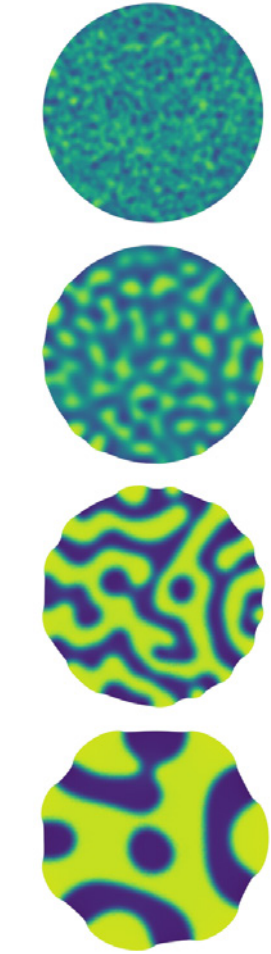
depending on the elastic deformation  $F_e = FF_p^{-1}$  in a multiplicative decomposition, where  $F_p$  describes inelastic effects,  $F = \mathbb{I} + \nabla \mathbf{u}$  is the deformation gradient expressed with the displacement  $\mathbf{u}$ . The dependence on an internal order parameter  $\varphi$ , e.g., representing chemical concentration of solvents or charges, accounts for the influence of a complex environment.

Minimizers of the free energy can give rise to phase separation and phase transitions, particularly in cases where  $W$  is non-convex, leading to highly non-unique minimizers. Consider the energy

$$W(F, \varphi, \nabla \varphi) = \frac{G}{2} (\text{tr}(\mathbb{C} - \mathbb{I}) - 2 \ln(\det F)) + \frac{\sigma}{2} |\nabla \varphi|^2 + \varphi \ln \varphi + (1 - \varphi) \ln(1 - \varphi) + \chi \varphi(1 - \varphi),$$

where  $\mathbb{C} = F^T F$ ,  $G$  encodes the shear modulus,  $\sigma$  represents an interface term, and the remaining terms describe a Flory–Huggins-type mixing entropy used for polymer mixtures. The parameter  $\chi$  controls the phase behavior:  $\chi < 0$  promotes mixing, while  $\chi > 0$  favors phase separation. The irreversible gradient flow dynamics of such a system is governed by a dissipation potential  $\Psi^*(q; \eta)$  that describes irreversible effects and leads to an evolution  $\partial_t q = D_\eta \Psi^*(q; -D_q \mathcal{F}(q))$  where the state  $q = (\mathbf{u}, F_p, \varphi)$  represents elastic displacements and inelastic deformations as well as scalar variables  $\varphi$ , describing an abstract but thermodynamically consistent dissipative dynamic, including phenomena such as viscous friction, viscoelastic relaxation, and phase separation or phase transition of sol and gel phase; see Figure 2. In particular, the bond reformation in the macroscopic gel leads to a relaxation of elastic stresses via the evolution of the inelastic variable  $F_p$ .

At WIAS, we have been investigating the energy-driven evolution of gels, proving the well-posedness of the resulting PDEs, modeling gel dynamics such as poroelasticity, phase transitions, and phase separation, as well as developing structure-preserving discretizations—and we continue to advance these research topics. These include finite element methods to approximate functionals in finite-dimensional subspaces, as well as time discretizations that respect the energy dissipation structure [1, 2]. These efforts in RG 1 *Partial Differential Equations* and RG 7 *Thermodynamic Modeling and Analysis of Phase Transitions* are aimed at biological applications in biomechanics and biomedicine in collaboration with researchers from Berlin Charité [3]. A key focus is on extending classical Kelvin–Voigt rheology of purely viscous solids to include viscoelastic relaxation of Maxwell type using gradient flows and GENERIC (General equation of non-equilibrium reversible irreversible coupling), to include the reformation of elastic crosslinks, which is joint work with Freie Universität Berlin (Andreas Zafferi) and Charles University Prague (Tomáš Roubíček) in the context of geophysical applications. Furthermore, currently extensions to charged polymers and conductive gels are explored as a natural extension of existing WIAS expertise [4, 5] on analysis, modeling, and simulation of charge transport and gelation on the particle level. The study of the gelation transition, in particular, represents a major milestone in this research with the University of Oxford (Andreas Münch, Sarah Waters), where insights from discrete particle systems are expected to play a critical role.



**Fig. 2:** Visualization of phase separation in a viscoelastic gel progressing over time from top to bottom. The gel exhibits volume changes (swelling), showing distinct swollen (yellow) and contracted (blue) phases. Image adapted from [2].

### Particle systems with coagulation

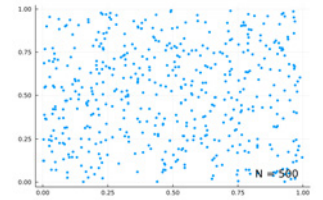
A complementary perspective on the phenomenon of gelation is developed within the research topic Coagulation. In contrast to the continuum approach, the research of RG 5 *Interacting Random Systems* is dedicated to stochastic models that contain individual descriptions of a large number of particles interacting via pairwise coagulations that take place over time. Coagulation refers to the merging of particles into a new particle and is modelled as an irreversible change of the particle system, distinguishing it from the bonding processes we described earlier. Through successive coagulations, increasingly larger structures emerge, which may lead to a gelation transition depending on whether the larger structures are visible on the macroscopic scale: a phenomenon interpretable as either a phase transition influenced by thermodynamic potentials or a kinematic transition governed by the rates of dynamic processes. This duality reflects the interplay between statistical mechanics and particle-level dynamics in gelation processes.

When aiming for rigorous results about the *gelation transition*, a tractable model has to be found. A probabilistic approach was chosen, following the idea of Particle-based Modeling, and a stochastic process for coagulation is defined. We neglect the movement of the particles, as well as their spatial extension or viscoelastic properties of the network, focusing instead on two properties: their *mass* and *location* in an abstract state space. The interacting forces that lead to coagulations are captured via a so-called *coagulation kernel*, which is a function determining the rate at which a particle pair merges or forms a bond based on the particle properties. A precise introduction to this model, the so-called *Marcus–Lushnikov process*, is given below.

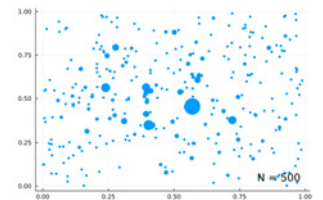
### Stochastic models for coagulation

**The inhomogeneous random graph.** A stochastic model for coagulation is given by a random graph, where edges are formed between its vertices over time, such that the clusters (i.e., connected components) of the graph can coagulate due to the addition of an edge. One initializes the process with  $N$  unconnected vertices, where each vertex  $v$  carries some spatial data  $x_v \in S$ . Then, an edge between a vertex pair with data  $x, x' \in S$  appears at rate  $\frac{1}{N} \kappa(x, x')$ . In Figure 5, we illustrate how the cluster configuration of the graph can change through the addition of an edge. The goal is then to study the evolution of the clusters of the graph for a large number  $N$ . We extensively studied this model in [6], where we provide a detailed analysis of the gelation transition that marks the emergence of a *giant* cluster whose number of vertices is proportional to  $N$ .

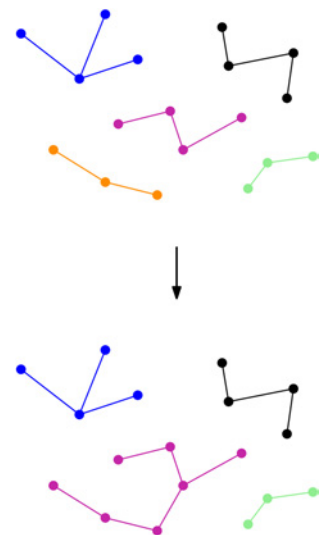
**The Marcus–Lushnikov process.** The Marcus–Lushnikov process is a stochastic process that models the evolution of particles that undergo successive coagulation events. The particle data is given by a location in an abstract space  $S$  and an integer mass. At time  $t \geq 0$ , the random configuration of the process is described by the collection  $(X_i(t), M_i(t))_{i=1}^{n(t)}$ , where  $(X_i(t), M_i(t))$  is the data of the  $i$ -th particle and the total number of particles at any time  $t$  is given by  $n(t)$ . Initially, the expected number of particles is given by  $N$  and each particle carries a mass that is equal to 1. Then, one samples random times for each particle pair that are independent and exponentially distributed. Their parameters depend on the data of the particle pair. More precisely, for a particle pair with data  $(x, m), (x', m') \in S \times \mathbb{N}$  the parameter is given by  $N^{-1} K((x, m), (x', m'))$ , where



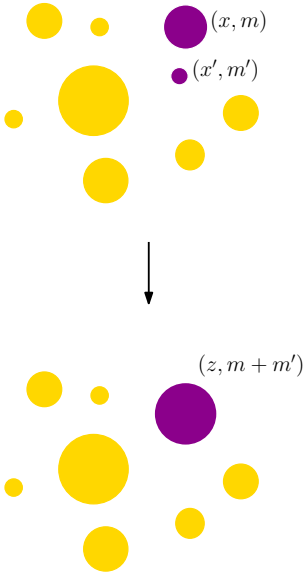
**Fig. 3:** Initial configuration of the coagulation process



**Fig. 4:** Configuration of the coagulation process after several coagulations took place



**Fig. 5:** Transition of the cluster configuration in the inhomogeneous random graph



**Fig. 6:** Transition of the particle configuration in one coagulation step

$K$  is the coagulation kernel. The smallest exponential time defines the first coagulation time and triggers a coagulation event. The corresponding particle pair is removed from the configuration and replaced by a new particle. For a coagulating particle pair with data  $(x, m), (x', m')$  the new particle is defined to have a mass  $m + m'$  and its new location  $z$  is sampled according to a distribution  $\Upsilon((x, m), (x', m'), dz)$  depending on the particle data. The transition of the configuration in a coagulation event is illustrated in Figure 6. We call  $\Upsilon$  the *placement kernel*. After the transition, the parameters of the exponential times are updated according to the new particle configuration and the procedure is iterated. As mentioned above this model focuses solely on the coagulation mechanism that can be observed in different physical or chemical systems. An obvious choice for the space  $\mathcal{S}$  would be  $\mathbb{R}^d$ , however, various choices are possible. For example, if one wants to model coagulation of molecules, then one can include geometric data or electrical charges into the particle description.

The main example that we have in mind is a coagulation kernel that has the form

$$K((x, m), (x', m')) = \varphi(x, x')mm', \quad \text{for } (x, m), (x', m') \in \mathcal{S} \times \mathbb{N},$$

where  $\varphi$  is a non-negative continuous function. More precisely, one can think of a function that only depends on the distance of the two particle locations  $x, x'$  and is bounded from above. The fact that the kernel grows bilinearly in the masses ensures that the interaction rate with particles of large masses grows sufficiently fast, as their mass grows. From easier, i.e. non-spatial, versions of the model it is known that this is the regime where gelation can be observed.

The *Marcus–Lushnikov process* is the empirical process  $\Xi^{(N)} = (\Xi_t^{(N)})_{t \geq 0}$ , where, for  $t \geq 0$ ,

$$\Xi_t^{(N)} = \sum_{i=1}^{n(t)} \delta_{(X_i(t), M_i(t))} \in \mathcal{M}(\mathcal{S} \times \mathbb{N}) \quad (1)$$

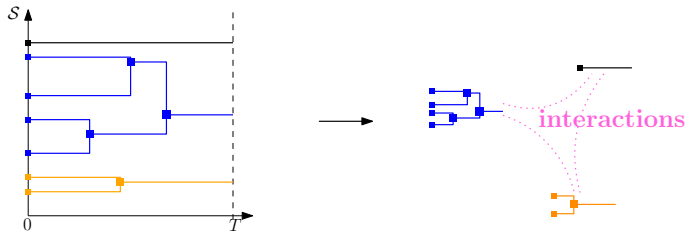
is the empirical measure registering the particle data at time  $t$ . For a large number of initial particles, i.e. for the limit, as  $N \rightarrow \infty$ , one is interested in understanding the limit of  $\frac{1}{N} \Xi^{(N)}$ .

### Large deviations approach to gelation

The usual approach to study the Marcus–Lushnikov process builds on its construction as a continuous-time Markov chain and aims to show that its limit, as  $N \rightarrow \infty$ , follows a certain dynamics, which can be described via a system of differential equations, called the *Smoluchowski equation*. However, it is known that this equation does not always have a solution, which is related to the possibility that after a finite time large particles are formed whose mass diverges as  $N \rightarrow \infty$ . If their masses make up a non-trivial portion of the entire mass in the system, we call the collection of those particles the *gel*. Unfortunately, the gel's influence on the system's dynamics is not captured in the Smoluchowski equation, and an extension of the equation is only possible in certain cases, giving the *Flory equation* or *modified Smoluchowski equation*.

We resort to an approach that describes all possible evolutions of the particle system by carefully studying the limit of the distribution of the process with the help of Large Deviations. A main challenge consists in finding a suitable description of the distribution and was solved in our work

[7] via a statistical mechanics approach that has not been used in that way before.



**Fig. 7:** Illustration of the decomposition of the process into three interacting coagulation trees

The key is to decompose the coagulation process into certain sub-processes, called *coagulation trees*, each of which tracks the evolution of particles that have coagulated by a fixed time  $T$  into one particle, see Figure 7. Thus, we reinterpret the outcome of the coagulation process on the time interval  $[0, T]$  as interacting coagulation trees that are sampled according to a certain distribution. They *interact* with each other via an interaction cost that corresponds to the probability that none of the particles in distinct trees have coagulated during  $[0, T]$ . This approach is not only novel, but it is useful for deriving a large-deviations principle that describes the limit of the distribution of  $(\frac{1}{N} \Xi_t^{(N)})_{t \in [0, T]}$ , as  $N \rightarrow \infty$ , on an exponential level. Let us explain briefly how the theory of large deviations sheds light on gelation. Indeed, it can be used to identify the optimal state of the system that can be observed with high probability, as  $N \rightarrow \infty$ . If the optimal state only consists of particles of finite mass, as  $N \rightarrow \infty$ , then gelation did not occur, while otherwise gelation did occur.

## Conclusions and outlook

In our work on PDEs for gels, we analyze and discretize models that incorporate poroelastic and viscoelastic properties grounded in thermodynamic principles [1, 2]. Moving forward, we aim to extend these models to account for more complex macroscopic aspects of gelation. In our work on the Marcus–Lushnikov process [7], we employ the large-deviations approach to derive criteria for gelation that depend on upper and lower bounds on the coagulation kernel. In our previous study on the inhomogeneous random graph [6], we were even able to determine a precise time of gelation and found a description of the spatial configuration of the macroscopic cluster. Several extensions of the model can be the subject of further investigations, e.g., allowing for fragmentation or movement of the particles.

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