# Non-equilibrium dynamics for chemical gelation processes

The Institute for Solid State Physics, Univ. of Tokyo
Kenji Ohira[1], Masatoshi Sato and Mahito Kohmoto

ゲルの物性を調べる手段として、その内部構造の研究が近年盛んに行われている。化学ゲルのゲル化過程では、結合の不可逆性からくる構造の凍結のため、内部構造を制御することが困難であり、ゲル化過程のダイナミクスを研究することが求められている。ゲルを構成するクラスターの不可逆な凝集過程を扱った最も簡単なモデルとしては、Diffusion Limited Cluster-cluster Aggregation (DLCA) model が挙げられる [1]。このモデルは、コロイドゲルに対して良い一致を与えるものの、高分子ゲルにおいてはクラスター内部の熱揺らぎによる運動を考慮していないため、扱う事ができない。そこで私達は、クラスター内部の熱揺らぎによる運動を導入したモデルを構築し、凝集過程におけるボンド揺らぎの効果を考察した。2次元格子上でシミュレーションを行ったところ、DLCA では得られない揺らぎに起因する多孔質構造が得られた。また、DLCA では存在しないゲル化臨界濃度の存在を示唆する事ができた。

Gels appear in a wide range of scientific areas; physics, chemistry, biology and so on. Moreover they have many important roles for technological applications. However, the nature of gelation, which determines structures of gels, is not completely understood. We need to study about dynamics of gelation to understand the properties of gels.

Dynamics of the chemical gelation depend on aggregation between clusters. Irreversible aggregation phenomena have been studied by the Diffusion Limited Cluster-cluster Aggregation (DLCA) model [1]. The DLCA model is rather simple, but it excellently reproduces properties of colloidal gels such as the fractal dimension of clusters, the time evolution of cluster radius and so on. For polymer gels, however, there are some results which can not be explained by the DLCA model. For example, all polymer gels have finite critical concentrations below which no gelation occurs, but the DLCA model has no critical concentration[2].

To resolve the problems, we take into account fluctuations of intra-clusters in addition to the aggregations of clusters in the gelation. Namely, we improved the Bond Fluctuation Model [3] so that it can describe the aggregations of clusters and studies the effects of the fluctuations of bonds in the gelation processes.

We performed simulations at various monomer concentrations; $\phi = 0.1 \sim 0.3$. On the contrary to the DLCA model, we found a finite critical concentration at $\phi \simeq 0.22$ in this model. Fig.1 shows typical snapshots of gelation processes. The snapshots at a high concentration ($\phi = 0.3$. Fig.1(a)-(c)) show how a sol-gel transition occurs in our model. Initially (Fig.1(a)), randomly distributed monomers are connected by bonds as the site percolation model. Then, the monomers aggregate and form clusters as is seen in Fig.1(b). The clusters have fractal

[1]E-mail: kohira@issp.u-tokyo.ac.jp

structures and the fractal dimension is $d_f \simeq 1.79 \pm 0.06$, which is almost the same as the DLCA. However, Fig.1(c) shows that the final structure is completely different from that of the DLCA: The fluctuations of bonds causes a porous structure in Fig.1 (c). On the other hand, no gelation occurs at a low concentration. (See Fig.1(d)-(f).) Fig.1(f) shows that the clusters have globular structures which come from the intra-cluster aggregation by the bond fluctuations. Because of the globular structures, the clusters can not spread over the system and so they can not become a gel.

I will give more details of our model numerical results in the poster.

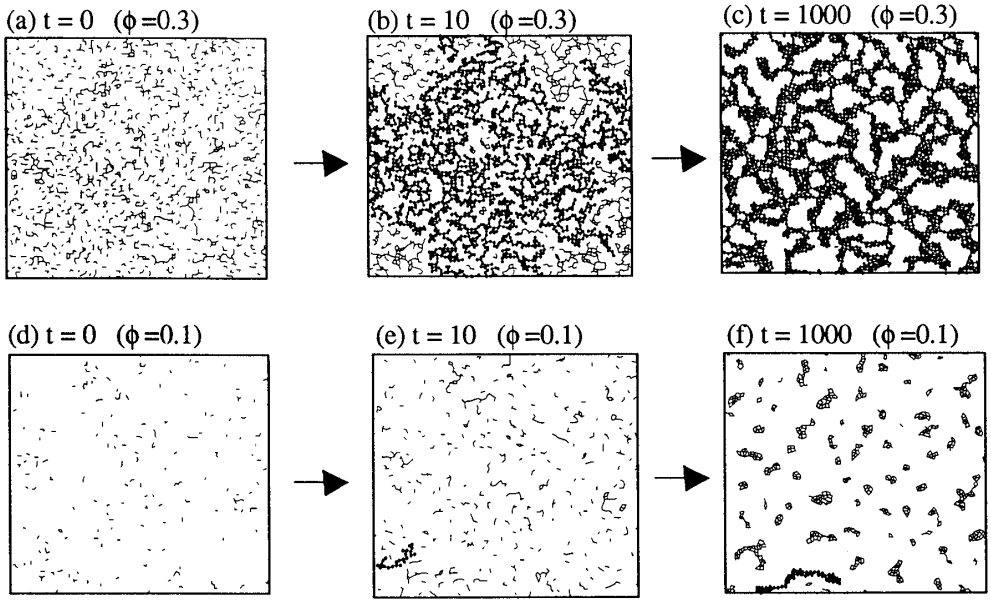


Figure 1: Snapshots of two gelation processes. $\phi$ is a monomer concentration and $t$ is a Monte Carlo step. The thin lines represent bonds and the black dots represent monomers in the largest cluster.

## References

[1] P. Meakin, Phys. Rev. Lett. **51**, 1119 (1983); M. Kolb, R. Botet and R. Jullien, Phys. Rev. Lett. **51**, 1123 (1983)

[2] J. C. Gimel, D. Durand and T. Nicolai, Phys. Rev. B **51**, 11348 (1995)

[3] I. Carmesin and K. Kremer, Macromol. **21**, 2819 (1988)