A mathematical characterization of the gel point in sol-gel transition

To cite this article: A H Bilge and O Pekcan 2015 *J. Phys.: Conf. Ser.* **574** 012005

A mathematical characterization of the gel point in sol-gel transition

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Abstract. We model the sol-gel transition in terms of Susceptible-Infected-Removed (SIR) and Susceptible-Exposed-Infected-Removed (SEIR) models and compare with experimental results. We show, numerically, that the "gel point" described as the onset of the gelation phenomena and measured experimentally, corresponds to an accumulation point of the extreme values of the derivatives of the gelation curve. We define the "critical point of a sigmoidal curve" as the limit of the points where the derivatives reach their extreme values, provided that this limit exists.

1. Introduction

Physical phenomena involving a phase transition are likely to be described by different mathematical models before and after the transition point. The polymerization of a monomer solution is such an example that displays the passage from the *sol* state to the *gel* state. In the sol state, monomers start to agglomerate, forming small clusters. There is a specific instant, called the *gel point* at which these clusters consolidate to form a giant network. In the steady-state, the gel fraction stabilizes to a value that may be less than 1, i.e, the sol and gel states may coexist. These transitions have been monitored and recorded by Pekcan and co-workers by a fluorescence technique for a variety of chemical and physical gels [1]. In most experiments, the sol-gel transition follows a sigmoidal curve with a sharp rise between the two stable states. At the exact instant of phase transition, physical properties of the monomer solution change; the gel point is either monitored by an independent experiment [2], or by finding the base point that gives the best fit to well-known power low growths [3]. The location of the gel point with respect to the inflection point of the sigmoidal curve is not fixed; in some types of experiments it is closer to the inflection point, in some other it is located earlier in time. Furthermore its location varies also with activation levels in the same experiment.

The Susceptible-Infected-Removed (SIR) and Susceptible-Exposed-Infected-Removed (SEIR) [8] epidemic models describe the spread of an infectious disease in a closed society. We have used these systems to model the gelation of sodium alginate-carragenan solution by fitting the curve for removed individuals to the gelation curve [4] for various levels of activation. We have noticed that the gelation curves obeying the "percolation model" and the "classical model" were described by the SIR and SEIR epidemic models respectively. This approach was motivated by the modeling of the sol-gel transition as a percolation model [5], [6], [7], providing a common basis with the spread of an epidemic in a closed society and the polimerization and gelation phenomena.

In the search for a description of the gel point in terms of the SIR and SEIR systems, we noticed that the points where the derivatives of the sigmoidal curve reach their global extremum formed a convergent sequence. We have used numerical techniques to compute the location of the limit point and we have observed that the location of the critical point agreed qualitatively with the gel point observed by dilatometric techniques [9]. Although we observed the existence of a limit point for the global extremum of the derivatives of a sigmoidal function for a variety of functions, the proof of this fact was extremely challenging. In [10] we have used Fourier and Hilbert transform techniques to prove the existence of a limit point of the global extreme values of a sigmoidal function under fairly general assumptions.

2. Epidemic models and the gelation mechanism

The Susceptible-Infected-Removed (SIR) and Susceptible-Exposed-Infected-Removed (SEIR) models describe the spread of an epidemic in a closed society. These models are based on a subdivision of the population into compartments, as indicated by the names of the models. It is assumed that the passage among the compartments are one-directional, i.e. in epidemiological framework, immunity, once acquired, cannot be lost. The strength of the epidemic depends both on the activity of the virus and on the level of interpersonal relations in the society. If the combination of these effects is strong enough, the number of infected individuals make a peak and then decrease steadily, as there are less and less susceptible individuals around [8].

In the Susceptible-Infected-Removed (SIR) model the time evolution of the number of "Susceptible (S)", "Infected (I)" and "Removed (R)" individuals is given by

$$\frac{dS}{dt} = -\beta IS, \quad \frac{dI}{dt} = \beta IS - \eta I, \quad \frac{dR}{dt} = \eta I, \tag{1}$$

where β and η are constants. In the SEIR model, the "Exposed (E)" individuals act as an intermediate step as seen from the equations below

$$\frac{dS}{dt} = -\beta IS, \quad \frac{dE}{dt} = \beta SI - \epsilon E, \quad \frac{dI}{dt} = \epsilon E - \eta I, \quad \frac{dR}{dt} = \eta I, \tag{2}$$

where β, ϵ and η are constants.

The link between epidemic spread and the gelation is the interpretation of both phenomena by "percolation" that typically represents the passage of gas or fluids trough porous media [11]. For the spread of a disease, susceptible individuals are analogous to empty sites while removed individuals are interpreted as filled sites of a percolating network. The passage from one state to the other is governed by the transition rules. Percolation models are built via simulations and take spatial evolutions into consideration. The SIR and SEIR models being systems of ODE's ignore spatial evolution of the disease and give only cumulative numbers.

3. The gelation of the polyacrilamide-sodium alginate composite

The sol-gel phase transition of polyacrilamide-sodium alginate composite with low and high Sodium Alginate concentrations is studied in [2]. The gelation curves for various levels of activation are presented in Figure 1. The steep, low amplitude curves correspond to low SA concentrations obeying percolation model. The slower rising high amplitude curves obey classical model.

In these experiments, the gel points are determined by a dilatometric technique. The critical point is located at the left of the inflection point of the gelation curve; it is farther away from the inflection point for high activation (low SA concentrations) levels).

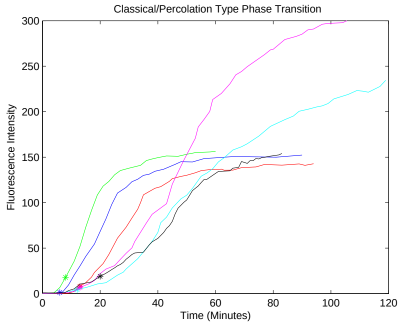

Figure 1. The gelation of the polyacrilamide-sodium alginate composite.

4. Derivatives of the gelation curve

In the search for a mathematical characterization of the gel point, we observed that successive derivatives of the sigmoidal curve representing the number of removed individuals seem to "diverge" near a point that agrees qualitatively with the "gel point" that has been experimentally determined. The mathematical set-up for this phenomenon is described below.

Let $y(x)$ be a smooth sigmoidal curve, i.e, monotone increasing with horizontal asymptotes as $t \to \pm\infty$ and let $\{x_{m,i}\}$ and $\{x_{a,i}\}$, $i = 1, 2, \dots$, be the set of points where the derivatives of odd and even order reach their extreme values. If the sequences $\{x_{m,i}\}$ and $\{x_{a,i}\}$ are both convergent and they have a common limit x_c, this limit is called "the critical point of the phase transition".

The ith zero of $y^{(n)}$ is x_n^i. The inflection point of $y(x)$ is the unique zero of its second derivative $y^{(2)}$, denoted by x_2^1. x_2^1 lies in between the two zeros of the third derivative x_3^1 and x_3^2, and we have the order relations $x_3^1 < x_2^1 < x_3^2$. The fourth derivative has three zeros, satisfying the order relations $x_4^1 < x_3^1 < x_4^2$, $x_4^2 < x_3^2 < x_4^3$. Although the zeros of the third and fourth derivatives alternate, we can't say anything about the relative positions of x_2^1 and x_4^2. Thus, the observed regular behavior of the zeros near the "critical point" is not a straightforward consequence of the alternation of zeros of successive derivatives. The extrema of odd derivative correspond to the zeros of even derivatives and vice versa. Thus, if the critical point is to represent some type of break-point, the best that we can expect is that the sequences, $\{x_{m,i}\}$ and $\{x_{a,i}\}$, converge to a common limit point x_c.

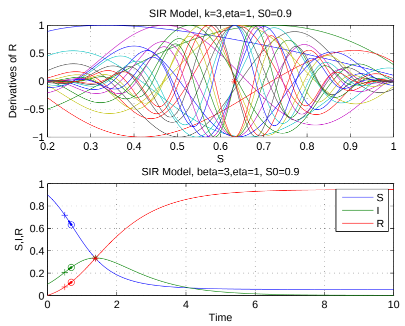

Figure 2. Derivatives of $R(t)$ for $k = \beta/\eta = 3$.

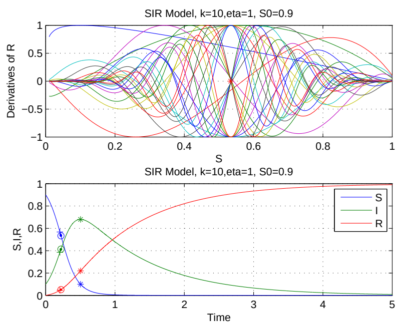

Figure 3. Derivatives of $R(t)$ for $k = \beta/\eta = 10$.

The first 24 derivatives of $R(t)$ normalized to 1 for $\eta = 1$, $S_0 = 0.9$ and $k = \beta/\eta = 3$ and $k = 10$ are plotted against $S(t)$, respectively in Figures 2 and 3. The phase transition points are indicated by ($*$) in the upper graphs. The lower graphs display the time domain plots of the solution curves S, I, R. $S(t)$ is monotone decreasing while $R(t)$ is monotone increasing. The sequence of points converging to the phase transition point t_c are shown on each curve by (.). The phase transition point t_c indicated by (o), is located between the maximum of zero I, t_m denoted by ($*$) and the inflection point of I, t_a denoted by (+). For $k = 3$, t_c is located at 78% left of t_m in the interval (t_a, t_m) The first 24 derivatives of $R(t)$ normalized to 1 for $k = 10$, $\eta = 1$ and $S_0 = 0.9$.

5. Dependency of the critical point on the system parameters

The relative position of the critical in the interval bounded by the zeros of the third derivative and the inflection point is shown in Figure 4, for $k = 3, 4, 5, 10$. In these figures, the inflection point, the zero of the third derivative and the critical point are shown respectively by ($*$), (+) and ($\circ$). It can be seen that, as k increases, the relative position of the critical point in between the zero of the third derivative and the inflection point is moving towards the zero of the third derivative, as the parameter k increases. For example for $k = 10$, the critical point t_c is located at 94% left of t_m in the interval (t_a, t_m).

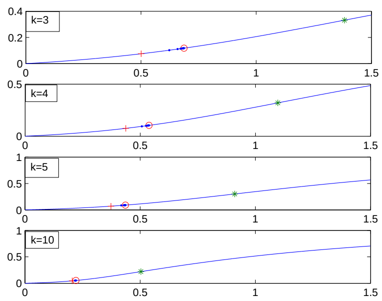

Figure 4. The location of the critical point.

References

[1] O.Pekcan and S. Kara, "Gelation Mechanisms", *Modern Physics Letters B*, 26 (27), 1230019 (2012).
[2] G.A. Evingur, F. Tezcan, F.B. Erim and O. Pekcan, *Monitoring the gelation of polyacrylamide-sodium alginate composite by fluorescence technique*, Phase Transitions, vol. 85, Issue 6, pp. 530-541, (2012)
[3] Y. Yilmaz, A. Erzan and O. Pekcan, Critical exponents and fractal dimension at the sol-gel phase transition via in situ flourescence eperiment, Phys. Rev. E, Third series, vol. 58, Issue 6 Part B, pp. 7487-7491, (1998).
[4] A.H. Bilge, O. Pekcan and V. Gurol, *Application of epidemic models to phase transitions*, Phase transitions, Volume 85, Issue 11, 2012 DOI:10.1080/01411594.2012.672648, pp 1009-1017.
[5] D. Stauffer, Introduction to Percolation Theory (Taylor and Francis, London, 1985).
[6] P. J. Flory, J. Am. Chem. Soc. vol. 63, p. 3083, (1941).
[7] W. H. Stockmayer, J. Chem. Phys. vol. 11, p. 45, (1943).
[8] H.W. Hethcote, *The mathematics of infectious diseases*, SIAM Rev. vol.42, pp.599-653, (2000).
[9] A.H. Bilge and O. Pekcan, *A mathematical Description of the Critical Point in Phase Transitions*, Int. J. Mod. Phys. C, vol. 24, 2013. International Journal of Modern Physics C, Volume 24, Issue 10, id. 1350065
[10] A. H. Bilge and Y. Ozdemir, Preprint: arXiv:1407.4839v1 [math.CA].
[11] D. Stauffer and A. Aharony, Introduction to Percolation Theory (Taylor and Francis, 43 London, 1992).