

Theoretical study on phase separation of electrolytes

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誘電率が大きく異なった2種類の液体の混合系（例えば水とアルコールの混合系）では、相転移の際に静電効果が大きな役割を果たす。さらに、水和の自由エネルギーは水の密度に強く依存することも、系の振る舞いに大きな影響を与える。2相系では、2成分の界面に電気2重層が形成されることは良く知られているが、その解析は局所的な誘電率が水の密度に大きく依存するため非常に難しい。この発表では、簡単な数理モデルに基づいたシミュレーションの結果をいくつか報告する。

1 Introduction

In binary mixtures of liquids with highly different dielectric constants, such as water and alcohol, electrostatic effect becomes prominent in phase separations. Moreover, free energy of hydration strongly depends on the density of water. In two-phase states, electric double layers are formed on the interface between two components. However, it is quite difficult to analyze the phase transition because the local dielectric constant depends on the density. In this presentation, we report results of a numerical simulations based on a simple mathematical model.

2 Model equations and numerical results

In our model, we introduce a free energy functional

$$F = \int d\mathbf{r} [f_0(\phi) + f_{\text{ion}}(n, \phi) + f_{\text{el}}(\phi, n)]. \quad (1)$$

The first term is the Bragg-Williams free energy (Flory-Huggins free energy)

$$\frac{f_0(\phi)v_0}{k_B T} = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) + \frac{C}{2}(\nabla \phi)^2. \quad (2)$$

The second term is the entropic contribution from the ion densities written as

$$\frac{f_{\text{ion}}(n, \psi)}{k_B T} = \sum_{\text{ions}} [n_i (\ln n_i - 1) - g_i \phi n_i], \quad (3)$$

where $-g_i \phi n_i$ is the hydration energy of ions depending on the local water density ϕ . The third term is the electrostatic free energy

$$f_{\text{el}}(\psi, n) = \frac{\epsilon(\phi)}{8\pi} \mathbf{E}^2, \quad (4)$$

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where $\epsilon(\phi) = \epsilon_0 + \epsilon_1\phi$ is an inhomogeneous dielectric constant. The electric field $\mathbf{E}$ is calculated by the Poisson's equation

$$\nabla \cdot \epsilon(\phi) \nabla \Phi = -4\pi \sum_{\text{ions}} Z_i e n_i, \quad \mathbf{E} = -\nabla \Phi. \quad (5)$$

We consider the binary mixture of the polar and non-polar solvents with two kinds of ions. Using the Cahn-Hilliard formulation, we write dynamic equations as

$$\frac{\partial \phi}{\partial t} = \nabla \cdot L(\phi) \nabla \frac{\delta F}{\delta \phi}, \quad \frac{\partial n_i}{\partial t} = \nabla \cdot \lambda(n_i) \nabla \frac{\delta F}{\delta n_i} \quad (i = 1, 2). \quad (6)$$

We numerically integrate above equations in 256×256 systems. If the difference of the solvation coefficient of ions g_i is large, we obtain spatially modulated patterns with a typical length in Fig. 1. In Fig. 2, we show the relation between the perimeter length and t . Compared to the model B, its time evolution is much slower due to the electrostatic interaction.

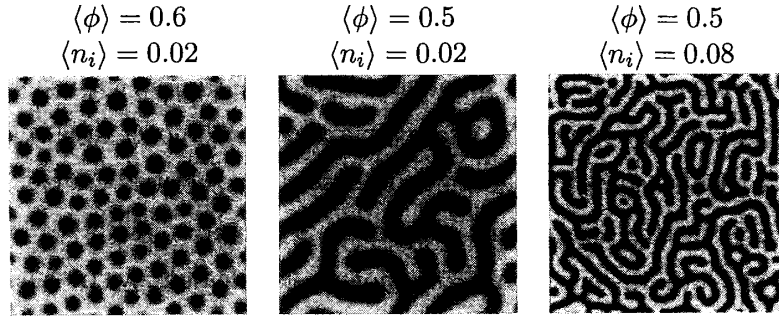


Figure 1: Spatially modulated patterns

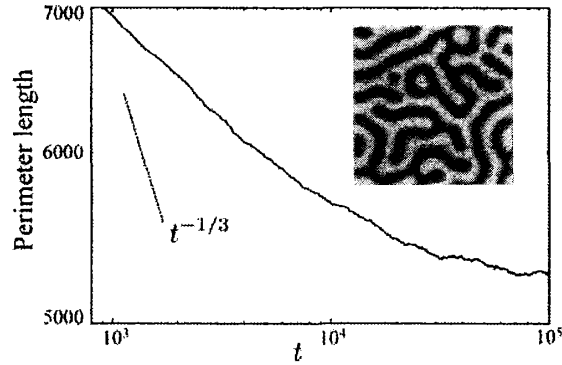


Figure 2: Relation between perimeter length and time t . Domain growth law is much slower than that of model B ($t^{-1/3}$).