Effects of hydrodynamic interactions on a coil-globule transition of a single polymer

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ソフトマターは，系の内部に溶媒を含んでいるため，流体を介した相互作用がそのダイナミクスに大きく影響している．本研究では，この流体力学的相互作用を取り入れたシミュレーション手法を用いて，流体が高分子鎖のコイル‐グロビュール転移において果たす役割について明らかにすることを目的とする．我々は，様々な慣性半径を持つ初期配置からの凝縮ダイナミクスを扱った．その結果，高分子鎖の初期配置によって流体は，大きく分けて２つの働きをすることがわかった．

A polymer immersed in a solvent begins to collapse from an expanded to a compact globule state, when the solvent quality changes from good to poor. This phenomenon is known as a coil-globule transition. The static property of this transition has been well understood theoretically and experimentally. Because of experimental difficulties, however, its dynamics is less understood. Since a coil-globule transition is regarded as a model of a protein folding, the understanding of the transition is also highly desired from the viewpoint of biophysics.

Soft condensed matters, such as polymer solution and colloidal suspension, often contain a solvent in it. The solvent affects not only the stability of the system but also its dynamics. Especially, hydrodynamic interaction (HI) via a solvent medium plays a key role in the dynamics of dilute polymer solutions. It has been reported that the HI accelerates the coil-globule transition of a flexible polymer and changes a transient morphology of the polymer in the process of the transition [1].

On the other hand, it is known that the HI slows down the dynamics of colloidal dispersions. For example, when two particles are approaching, the solvent between them has to be squeezed out. This squeezing flow effect increases the viscosity of the suspension. One of us (H. Tanaka) predicted that HI not only accelerates the coil-globule transition, but also retards it via a squeezing flow effect [2]. We show results of coarse-grained simulations of a coil-globule transition of a single polymer, focusing on these roles of HI.
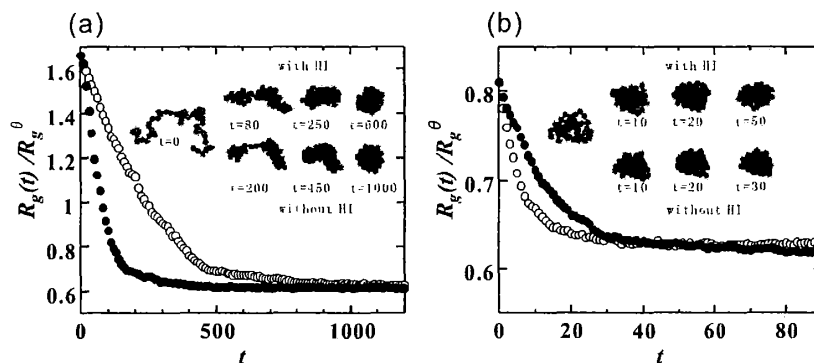

Figure 1: Temporal changes of the gyration radius R_g. (a) For a case where the initial $R_g(0)$ is larger than R_g^θ. (b) For a case where the initial $R_g(0)$ is smaller than R_g^θ. • and ○ correspond to the case with HI and without HI, respectively. Typical configurational changes of the polymer are also shown in the inset.

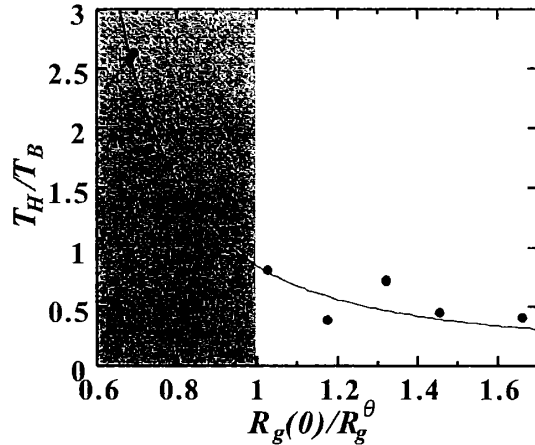[1] E-mail: kamakama@iis.u-tokyo.ac.jp

Figure 2: Variation of the ratio of T between T_H and T_B versus the scaled initial gyration radius $R_g(0)/R_g^\theta$

We perform coarse-grained simulations by means of Fluid Particle Dynamics method (FPD) [3]. To elucidate the effects of HI, we also perform Brownian Dynamics simulation (BD), which interacts solvent only through Brownian noise and frictional force, and compare the results with those of FPD simulations with HI.

Figure 1(a) shows the temporal changes in gyration radius $R_g(t)$ of a collapsing polymer for a case where the initial gyration radius $R_g(0)$ is larger than that of an ideal chain at θ-solvent R_g^θ. It indicates that the HI not only accelerates the coil-globule transition of the polymer as reported previously [1], but also affects the kinetic path. If the HI is absent, some clusters form by parts of the chain and they grow with time by absorbing the slack polymer. On the other hand, the polymer forms a rod (or sausage)-like shape and it shrinks into a globule rather smoothly with HI. The elongated structure is less resistive against viscous friction from the solvent and collapses quickly. Figure 1(b) shows the development of a collapsing polymer when $R_g(0)$ is smaller than R_g^θ. Here we cannot see a distinguished difference in the configurational change between the cases with HI and without HI. The polymers have compact rounded structures initially and they collapse into globules rather isotropically. Interestingly, the HI slows down the transition. This is because the solvent contained in the coil of the initial state has to be squeezed out and this leads to the viscous friction against the transition.

Since the gyration radius fluctuates by the thermal noise, it is not a good measure to define the characteristic time of the transition. So, we define a parameter $T = \int_0^\tau (R_g(t) - R_g(0))dt$ to characterize the transition. Figure 2 plots the ratio of T between the cases with HI (T_H) and without HI (T_B) against the scaled initial gyration radius $R_g(0)/R_g^\theta$. It shows that the HI accelerates the transition when $R_g(0) > R_g^\theta$, whereas it slows down the transition when $R_g(0) < R_g^\theta$. The HI also changes the kinetic pathway of the transition, as shown in the inset of Fig. 1(a). This implies the polymer can escape from a local energy minima in the energy landscape of the coil-globule transition with a help of HI.

References

[1] N. Kikuchi, J. F. Ryder, C. M. Pooley and J. M. Yeomans, Phys. Rev. E. **71**, 061804 (2005).

[2] H. Tanaka, J. Phys.: Condens. Matter **17**, S2795-2803(2005)

[3] H. Tanaka and T. Araki, Phys. Rev. Lett. **85**, 001338 (2000).