Universality of viscoelastic phase separation in soft matter

2005 J. Phys.: Condens. Matter 17 S3195

(http://iopscience.iop.org/0953-8984/17/45/002)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) S3195–S3204 doi:10.1088/0953-8984/17/45/002

Universality of viscoelastic phase separation in soft matter

Hajime Tanaka, Takeaki Araki, Takehito Koyama and Yuya Nishikawa

Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

E-mail: tanaka@iis.u-tokyo.ac.jp

Received 22 September 2005
Published 28 October 2005
Online at stacks.iop.org/JPhysCM/17/S3195

Abstract

Recently we found that viscoelastic phase separation (VPS) is observed not only in polymer solutions, but also in protein solutions and colloidal suspensions. This suggests that VPS may be universally observed in any dynamically asymmetric mixture composed of slow and fast components. Such mixtures are ubiquitous in soft matter. The common feature of VPS is the formation of a transient gel made of the slow components just after a temperature quench into an unstable region of a phase diagram. Transient gelation is induced by deformation fields induced by phase separation itself; thus, it is a self-induced shear-thickening phenomenon. The connectivity of a transient gel causes the stress against diffusion-type deformation upon phase separation and thus leads to a strong coupling between the mechanical stress and the diffusion of particles: phase separation (or diffusion) can proceed only with the local breakup of a transient gel and the resulting loss of the connectivity. We argue that VPS is the fracture process of a transient gel induced by the self-generated mechanical stress due to interparticle attractive interactions. A simple toy model supports this scenario.

(Some figures in this article are in colour only in the electronic version)

M Supplementary data files are available from stacks.iop.org/JPhysCM/17/S3195

1. Introduction

Phase separation is one of the most fundamental phenomena responsible for the formation of heterogeneous structures in condensed matter and also in nature [1, 2]. It is commonly observed in various kinds of material including metals, semiconductors, simple liquids, and complex fluids such as polymer solutions, colloidal suspensions, emulsions, and protein solutions. Phase separation in condensed matter has so far been classified into two types: solid and fluid phase separation. For the former the only transport process is material diffusion, while for

the latter the material can be transported not only by diffusion, but also by hydrodynamic flow driven by the motion of the interface. It has been established that the phase-separation behaviour of solid (or fluid) mixtures can be described in a universal manner within the same category, irrespective of the details of material. This allows us to predict the kinetics of pattern evolution. This predictive power is extremely useful for our material design.

It is known for the above types of phase separation [1, 2] that depending upon the composition of a mixture, phase separation produces either a bicontinuous or droplet pattern. There a pattern coarsens to lower the interface energy and the domain shape is determined by the force acting on the interface. Some time ago, however, we found [3–6] that phase separation can also produce a network pattern in polymer solutions, contrary to the above-mentioned conventional wisdom. In this case, the pattern is selected to satisfy the mechanical force balance condition, reflecting the viscoelastic nature of the polymer-rich phase. This type of phase separation is called 'viscoelastic phase separation (VPS)' [5, 6]. We suggested that the only requirement for the occurrence of VPS is the dynamic asymmetry between the components of a mixture and showed that VPS can also occur in a mixture whose components have very different glass-transition temperatures [7].

If this scenario is true, the similar phase-separation behaviour should also be observed in other types of soft matter such as colloidal suspensions, since they are a mixture of large particles and small liquid molecules and thus they have intrinsic 'dynamic asymmetry' between the components of a mixture, reflecting their size disparity. Thus, we proposed [8, 9] that VPS should be observed in colloidal suspensions, protein solutions, and emulsions. Indeed, there exist many experimental and numerical pieces of evidence that colloidal suspensions [10–19], protein solutions [12, 20, 21], and emulsions [22–25] form transient gel upon phase separation. However, there were no experimental studies convincingly supporting our argument. Currently, phase separation of these systems is actively discussed in relation to the slow dynamics associated with the glassy nature of a gel-like phase [26–28]. The relevance of our conjecture, or the importance of viscoelastic effects in a suspension of particles in a liquid, might be questioned due to the following fact: polymers have large internal elastic degrees of freedom, while colloids and proteins do not. The large internal degrees of freedom allow even individual polymer chains to bear mechanical stress under strain fields. In contrast, individual colloidal particles cannot bear any stress. Furthermore, entanglement effects play crucial roles in the rheological behaviour of polymers [29], but they do not exist in colloidal suspensions and protein solutions. These differences may give an impression that viscoelastic effects are not so important in phase separation of colloidal suspensions and protein solutions.

Very recently, however, we have found that VPS really occurs in colloidal suspensions [30] and protein solutions [31]. Here we review the characteristic features of VPS found in these mixtures and discuss the universal nature of VPS for three different systems: dilute polymer solutions, colloidal suspensions, and protein solutions. We also discuss the origin of viscoelastic effects in these examples, in which entanglement effects play no role, based on the results of our experiments and numerical simulations.

2. Experimental details

2.1. High-speed confocal microscopy observation

We observe a 3D pattern evolution process during phase separation with confocal fluorescent microscopy (Yokogawa Electric Co., CSU21, excitation wavelength 532 nm), equipped with a high-speed CCD camera (Vision Research, Inc., Phantom V4.1) (see figure 1(a)). We control the confocal microscopy, the camera, the piezo-focusing system (Physik Instrum., E-662 LV),

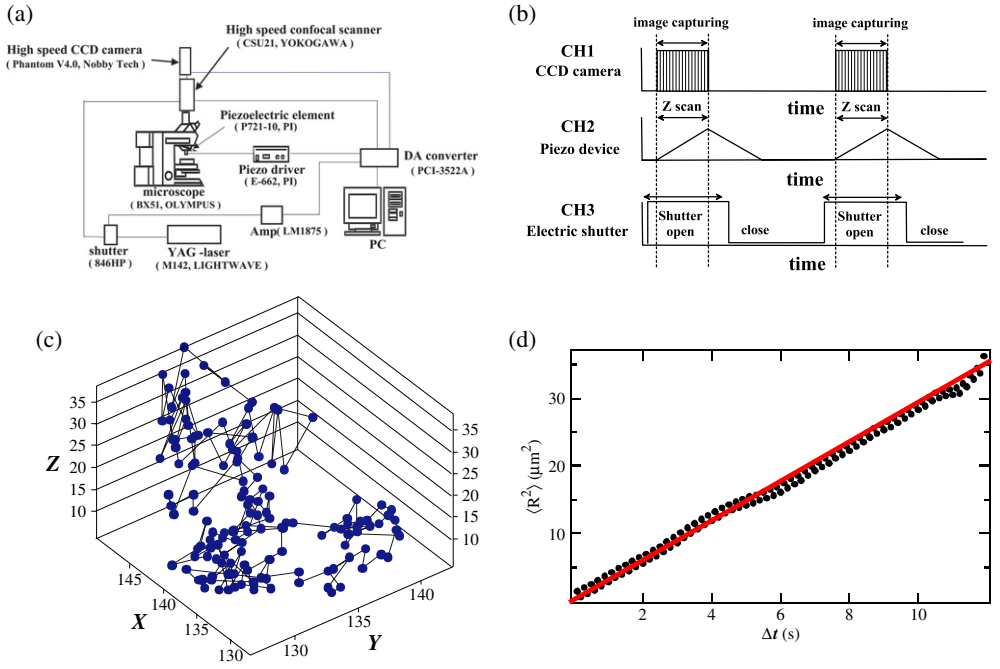

Figure 1. (a) Block diagram of a high-speed confocal microscopy system. (b) Timing chart for the control of the camera, the piezo focusing system, and the electric shutter. (c) A trajectory of the Brownian motion of a colloidal particle. The location of the particle is followed with a time resolution of 50 ms. One pixel corresponds to 0.16 μm. (d) Mean square displacement of a colloidal particle obtained by averaging six measurements. Each measurement has a duration of 8 s.

and the electric shutter (Newport Co., 846HP) in a coherent manner by electronic signals (CH1–CH3) from a digital–analogue (DA) convertor of a computer (see figure 1(b)) to obtain a 2D image (512 × 512) every 1 ms [30].

Figure 1(c) shows a trajectory of Brownian motion of a colloidal particle (diameter 1.0 μm) suspended in water, which was observed with an oil immersion 100× objective lens. Figure 1(d) plots the mean square displacement $\langle R^2 \rangle$ as a function of Δt, which was averaged for six measurements. From the relation $\langle R^2 \rangle = 6D\Delta t$, we obtain the diffusion constant D as 4.5×10^{-9} cm^2 s^{-1}. According to our dynamic light scattering measurements for a dilute suspension of the same colloidal particles, on the other hand, we obtain $D = 4.4 \times 10^{-9}$ cm^2 s^{-1}. This indicates that our confocal microscopy is indeed able to directly track the 3D coordinate of a Brownian particle with a time resolution of 50 ms. Our high-speed confocal microscopy allows us to capture a 3D image (consisting of 100 2D images: 409.6 μm × 409.6 μm × 80 μm with a resolution of 0.8 μm) within 100 ms. This ability is essential in obtaining a 3D phase-separation pattern at a certain time without distortion due to motion during the scanning period.

2.2. *Polymer solutions*

The polymer solution used was a mixture of monodisperse polystyrene and diethyl malonate. It was confined in a thin glass cell with a thickness of 10 μm. The phase-separation process was observed with phase-contrast microscopy. The temperature was controlled within ±0.1 K by a computer-controlled hot stage (Linkam LK-600PH) with a cooling unit (Linkam L-600A).

2.3. Protein solutions

The protein used was lysozyme (Wako Pure Chem. Ltd), whose molecular weight M_w is 14 300. Lysozymes were dissolved in a 50 mM buffer solution of sodium acetic acid and then its pH was controlled to be 4.0 by adding a small amount of HCl to it. We also added NaCl to screen the electrostatic interactions between protein molecules. Here we show results of samples containing 7.5 wt% NaCl. The sample was sandwiched between two cover glasses by using monodisperse glass beads as spacers. For 2D observation, the sample thickness was set to be 10 μm. For 3D observation, on the other hand, it was set to be 50 μm. See [31] for details, including the phase diagram.

For 3D observation, we used EOSIN Y (Polyscience, $M_w = 691$) as the fluorescent dye for lysozyme. Its excitation wavelength is about 520 nm, and its fluorescent wavelength is about 550 nm. It is trapped efficiently in the hydrophobic pocket of the protein. We note that EOSIN Y changes the location of the binodal line. For example, the binodal line was shifted to 43.5 °C from 36 °C at $\phi = 150$ mg ml^{-1}. This is because EOSIN Y is a salt and it screens the electrostatic interactions between proteins.

2.4. Colloidal suspensions

We used fluorescent polystyrene latex particles (Polyscience, monodisperse polystyrene latex containing rhodamine, diameter = 50 nm) as charged colloids, and NaCl as a salt. The observation was made with the above-mentioned confocal microscopy system. For microscopy observation, we matched the density of colloids (1.05 g cm^{-3}) with that of a salt solution by appropriately mixing H_2O (1.00 g cm^{-3}) with D_2O (1.10 g cm^{-3}) to avoid the gravity effects and prevent sedimentation. Then the phase separation is initiated by injecting salt into a sample. This is practically realized by contacting the bottom surface of a sample cell (thickness = 0.1 mm), which is made of an osmotic membrane, to an aqueous salt solution in the large reservoir at $t = 0$. This osmotic salt injection method enables us to initiate phase separation homogeneously *without inducing flow*. The characteristic time of salt diffusion over the cell is estimated to be $\sim$10 s, using the salt diffusion constant of $\sim 80 \times 10^{-7}$ cm^2 s^{-1}. This is fast enough to study the initial stage of phase separation. Phase separations in a colloidal suspension have so far been initiated by directly mixing it with either a polymer solution (for a colloid–polymer mixture) or a salt solution (for a charged colloidal suspension). It takes a rather long time to homogeneously mix them and, furthermore, flow induced by mixing strongly disturbs pattern evolution. Thus, it has been quite difficult to study the initial stage of phase separation. Our new method allows us to investigate the initial stage of phase separation without suffering from these problems. The interactions between colloids can be controlled by the amount of salt injected. According to the DLVO theory [10], the energy barrier for aggregation is estimated as $\sim 12\ k_BT$ for $\phi_s = 1.0$ wt%, $\sim 1\ k_BT$ for $\phi_s = 5.0$ wt%, and it disappears for higher ϕ_s. Once this barrier is overcome, the particles strongly attract each other with an energy of $\sim 20\ k_BT$. See [30] for details, including the phase diagram.

3. Experimental results

3.1. Polymer solutions

The phase-separation process observed in a dilute polymer solution under a deep quench is shown in figure 2(a). See also [32] and the supplementary video of [30]. Just after the quench, polymer-rich droplets are first formed by droplet spinodal decomposition and then their aggregation leads to the formation of a 'mesoscopic' network structure. We note that

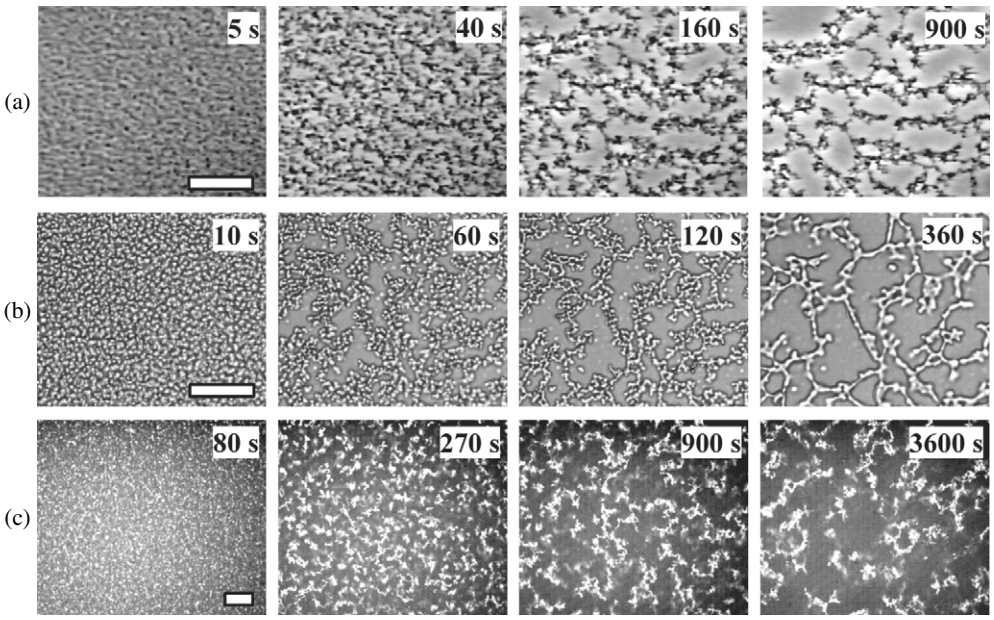

Figure 2. Comparison of pattern evolution observed in (a) a dilute polymer solution, (b) a protein solution, and (c) a polymer solution. The scale bar corresponds to 50 μm for (a)–(c). (a) is observed in a mixture of polystyrene (its molecular weight being 706 000) and diethyl malonate (0.5 wt% polystyrene) at $T = -20\,^{\circ}$C with phase-contrast microscopy. (b) is observed in a protein solution ($\phi = 200$ mg ml^{-1}, salt concentration 7.5 wt%) at 37 °C with conventional optical microscopy. (c) is observed in a colloidal suspension ($\phi = 0.25$ v%, $\phi_s = 15$ wt%) with confocal microscopy.

this two-step formation of a transient gel is different from the one-step transient gel formation observed in a nearly critical polymer solution. Reflecting this two-step process, the thickness of network arms is comparable to the size of initially formed droplets. The interface of the network is rather rough, reflecting this two-step process. Since polymer-rich balls are formed prior to network formation (or transient gel formation), the process resembles the network formation of colloidal suspensions (see figure 2(c) and below).

3.2. Protein solutions

The phase-separation behaviour in a quasi-2D geometry is shown in figure 2(b), while that in a 3D sample is shown in figure 3. We can clearly see the network formation of the protein-rich phase. In the video (see supplementary information), we show the phase-separation process of a protein solution (150 mg ml^{-1} lysozyme and 7.5 wt% NaCl). The quench depth from the binodal temperature was 1.5 K. The scale bar corresponds to 50 μm. Here the frame rate is accelerated by a factor of 4.

For a protein solution, a transient gel also seems to be formed by two steps, as in the case of the above dilute polymer solution: first small droplets are formed and then subsequently they form a network by their aggregation. In the early stage, the interface of the network is rough, but in the late stage it gradually becomes smoother due to the action of the interface tension. In the coarsening process, we can clearly see that the network coarsens to satisfy the mechanical force balance condition. The elementary process of network coarsening is the breakup of the backbone of the network. The coarsening proceeds by repeating the following

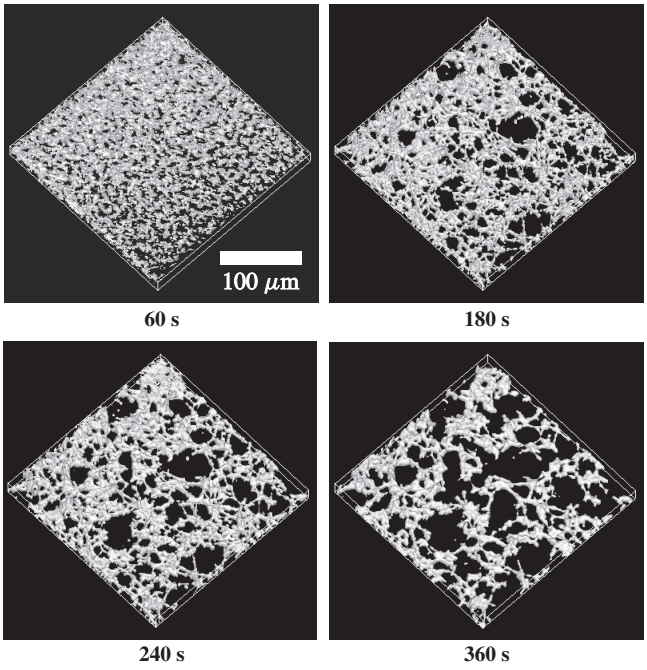

Figure 3. Temporal change in 3D phase-separation patterns during phase separation observed at $T = 41\,^{\circ}\mathrm{C}$ for $\phi = 150$ mg ml^{-1} and 7.5 wt% NaCl (240 μm $\times$ 240 μm $\times$ 20 μm). The quench depth measured from the binodal line is 2.5 K for this case.

process: the stress concentration on a weak part of the network, its breakup, and the resulting viscoelastic relaxation towards the metastable configuration satisfying the local force balance.

3.3. Colloidal suspensions

The phase-separation behaviour in a quasi-2D geometry is shown in figure 2(c), while that in a 3D sample is shown in figure 4. We can also see the network formation of the colloid-rich phase and its temporal coarsening. Our numerical simulation study suggests [33] that hydrodynamic effects between particles may help the formation of a transient gel (or percolation network). To characterize this, we estimated the fractal dimension d_{f} from the relation $N(R) \propto R^{-d_{\mathrm{f}}}$ by counting the number of lattices belonging to particles $N(R)$ contained in a sphere of radius R. The d_{f} is 2.0–2.4 at a short distance, but it tends to be 3 at a long distance, which means that the structure is isotropic at a large distance.

In the above case, the depth of the attractive potential may be far beyond 10 $k_{\mathrm{B}}T$ (k_{B}: Boltzmann's constant; T: temperature). This may give an impression that the network may be permanent and should not coarsen with time. However, we emphasize that the action of mechanical stress may entirely change the situation. The effective potential can be lowered by the elastic energy stored by the deformation of the backbone [8, 9]. The excess energy stems from the interactions among many particles on the interface. Thus, if it is concentrated on a few particles in a weak part of the network, the elastic energy can easily exceed the local adhesive energy supporting that part. Note that larger adhesive energy means larger interfacial energy and larger elastic energy. This mechanism leads to successive breakage of the stress-bearing backbone so long as the self-generated stress is strong enough to break up the backbone. The origin of the mechanical stress is the attractive interaction among particles.

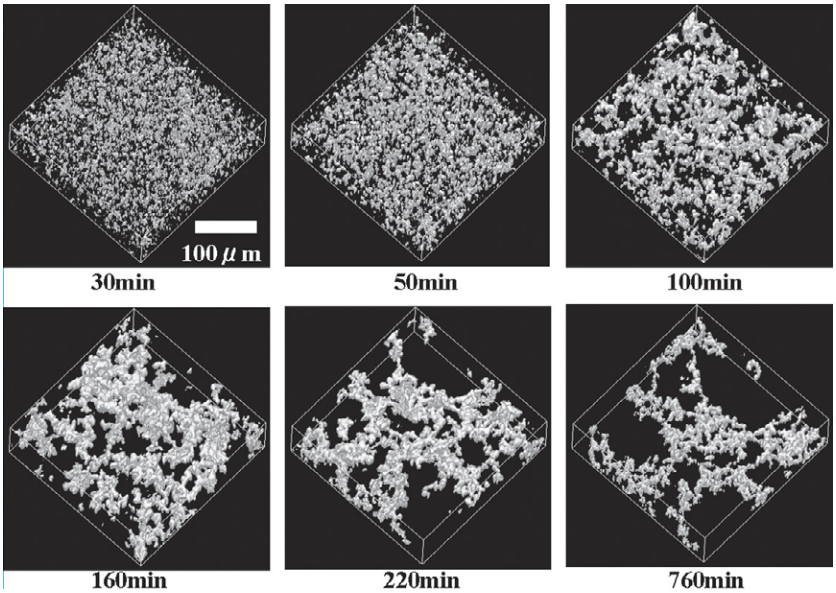

Figure 4. Temporal change in 3D pattern evolution during phase separation of a colloidal suspension ($\Phi_V = 0.1$ v%, $\phi_s = 4$ wt% NaCl). z was scanned over 80 μm with the resolution of 0.8 μm.

4. Universality and the origin of viscoelastic effects

As shown in figure 2, the patterns observed in dilute polymer solutions, protein solutions, and colloidal suspensions and their temporal changes are strikingly similar to each other. This strongly suggests that (i) the network-forming phase separation observed in protein solutions and colloidal suspensions should be classified as VPS, and (ii) VPS may be universal for any dynamically asymmetric mixtures. These results also suggest that the formation of a transient gel is crucial for VPS. Transient gelation is a consequence of large size disparity between the components of a mixture. It can be understood as shear thickening due to deformation fields induced by phase separation itself. It is the connectivity in this transient gel that prevents simple diffusion-dominated phase separation. We emphasize that the viscoelastic properties originate from the connectivity of a transient gel itself. This means that an individual particle need not have elastic degrees of freedom. This may be the case for colloidal suspensions. Although polymers and proteins have elastic degrees of freedom, they first form droplets and the transient gel is subsequently formed by aggregation of these droplets. Thus we may say that the viscoelastic nature of the phase separation described in this paper mainly stems from the viscoelastic properties of a transient gel itself rather than those of individual molecules. Since viscoelastic effects play a key role in phase separation of these mixtures, the phase-separation behaviour may be classified as VPS [8, 9, 30].

5. Physical factors separating a transient gel from a permanent gel

Here we briefly discuss what physical factors separate a transient gel from a permanent gel, since we observe both types of gel state for protein solutions and colloidal suspensions. We note that we observe only a transient gel for the polymer solution; in other words, the polymer-rich

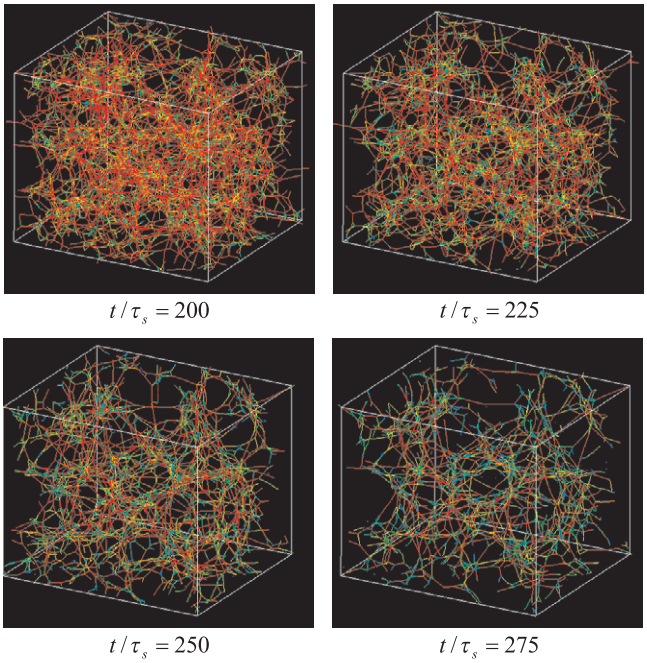

Figure 5. Evolution of a 3D network pattern of disconnectable springs as a function of the scaled time t/τ_s. We can see that the coarsening proceeds as a result of the disconnection of springs. τ_s is a characteristic time of the motion of a particle connected by a spring. The colour represents the strength of the mechanical force. For example, bright (red) parts are under strong stretching force.

phase behaves as liquid in the final stage. For both protein solutions and colloidal suspensions, an apparently permanent gel appears in a higher concentration of the slow component and in a lower (effective) temperature than a transient gel. The former is related to the stored elastic energy upon the formation of a network structure: the lower the concentration is, the higher the initially stored elastic energy is and thus a network cannot be stable. The latter, on the other hand, is related to the relative strength of the interparticle adhesion energy: the lower the temperature is, the stronger the adhesion force is. Thus, a network may be stable. These two factors naturally explain why a transient gel is formed at a lower concentration and a higher temperature. This simply tells us that if the elastic stretching force wins over the adhesion force, a network cannot support the stress and breaks up eventually. This scenario suggests that there is a possibility that a transient gel transforms into a permanent gel in the late stage of phase separation when the adhesion force wins over the stretching force; before the ergodic-to-nonergodic transition the coarsening can proceed, but after that the phase-separation structure is frozen. Such behaviour is indeed observed in protein solutions [31]. This problem will be discussed in more detail in the future.

6. A toy model supporting our scenario

As discussed above, the key of VPS is a transient gel state, which is characterized by the connectivity of the slow components and the stored elastic energy. Thus, we express a transient gel state by coarse-grained Brownian particles connected by disconnectable springs, which are under tension [34]. We employ a Brownian dynamics simulation since we deal with coarse-

grained effective particles immersed in a solvent in the overdamped limit. Effects of the solvent are represented by a hydrodynamic drag force and a random Brownian force acting on particles. The equation of motion for particle i is then given by

$$\zeta \frac{\mathrm{d}}{\mathrm{d}t}\vec{r}_i = -\frac{\partial}{\partial \vec{r}_i} U\{\vec{r}_i\} + \vec{\xi}_i, \tag{1}$$

where $\vec{r}_i$ is the position of particle i and ζ represents the friction constant. $\vec{\xi}_i$ is the thermal noise force, which satisfies the fluctuation–dissipation theorem. We assume that particles interact not only with the Lennard-Jones potential, but also via the disconnectable spring: $U\{\vec{r}_i\} = U_{\mathrm{LJ}}\{\vec{r}_i\} + U_{\mathrm{sp}}\{\vec{r}_i\}$, where $U_{\mathrm{LJ}}\{\vec{r}_i\}$ is a Lennard-Jones potential and $U_{\mathrm{sp}}\{\vec{r}_i\} = \frac{1}{2}k\Sigma'_{j(\neq i)}|\vec{r}_i - \vec{r}_j|^2$ (k being a spring constant). The latter interaction mimics the connectivity of a transient gel. Our spring is disconnected probabilistically with a rate $p(l)$ (l being the length of a spring) that increases with an increase in the mechanical stress. Thus, the elementary coarsening process of this spring network is the stress concentration on a weak part, its disconnection, and the relaxation to a metastable configuration. The coarsening proceeds by repeating this process. The details of the model and the results will be described elsewhere [34]. Here we just show the 3D coarsening process of a network of disconnectable springs storing the elastic energy. Although the model may be too simplistic, it captures the essential process of the coarsening of VPS and thus the pattern captures the important features of the network during the coarsening. This simulation result supports our scenario that VPS is the fracture process of a transient gel induced by the self-generated mechanical stress due to interparticle attractive interactions.

7. Summary

We demonstrated by both experiments and simulations that transient gelation and the resulting connectivity of the slow components of a mixture are essential for VPS. Dynamic asymmetry, or, more specifically, size disparity, of the components of a mixture is the cause of transient gelation and thus VPS. Nature selects a pathway of forming a stress-bearing configuration of the slow components of a mixture upon phase separation. This novel kinetic pathway of phase separation may play crucial roles in our basic understanding of complex phase ordering of soft matter, including foods and biological systems. VPS is not limited to polymeric mixtures, but is universal to any dynamically asymmetric mixtures including protein solutions and colloidal suspensions, as shown in this paper: the viscoelastic nature of the component of a mixture itself is not necessary for the occurrence of VPS. We note that the necessary condition for aggregation and gelation is the size asymmetry between the components. Our study may shed new light on the relationships among aggregation, phase separation, and gelation. VPS may play crucial roles in network formation in nature and condensed matter, particularly, in soft and bio-matter.

Acknowledgments

The author (HT) is grateful to W C K Poon for valuable discussion on transient gelation in colloidal suspensions and protein solutions. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] Onuki A 2002 *Phase Transition Dynamics* (Cambridge: Cambridge University Press)
[2] Gunton J D, San Miguel M and Sahni P 1983 *Phase Transition and Critical Phenomena* vol 8, ed C Domb and J H Lebowitz (London: Academic)

[3] Tanaka H and Nishi T 1988 *Japan. J. Appl. Phys.* **27** L1787
[4] Tanaka H 1992 *Macromolecules* **25** 6377
[5] Tanaka H 1993 *Phys. Rev. Lett.* **71** 3158
[6] Tanaka H 1994 *J. Chem. Phys.* **100** 5323
[7] Tanaka H 1996 *Phys. Rev. Lett.* **76** 787
[8] Tanaka H 1999 *Phys. Rev.* E **59** 6842
[9] Tanaka H 2000 *J. Phys.: Condens. Matter* **12** R207 and the references therein
[10] Russel W B, Saville D A and Schowalter W R 1989 *Colloidal Suspensions* (Cambridge: Cambridge University Press)
[11] Anderson V J and Lekkerkerker H N W 2002 *Nature* **416** 811
[12] Poon W C K 2002 *J. Phys.: Condens. Matter* **14** R859
[13] Verhaegh N A M, Asnaghi D, Lekkerkerker H N W, Giglio M and Cipelletti L 1997 *Physica* A **242** 104
[14] Verhaegh N A M, Asnaghi D and Lekkerkerker H N W 1999 *Physica* A **264** 64
[15] Soga K G, Melrose J R and Ball R C 1999 *J. Chem. Phys.* **110** 2280
[16] Noro M G, Kern N and Frenkel D 1999 *Europhys. Lett.* **48** 332
[17] Potanin A A, Derooij R, Van den Ende D and Mellema J 1995 *J. Chem. Phys.* **102** 5845
[18] Evans R M L and Starrs L 2002 *J. Phys.: Condens. Matter* **14** 2507
[19] Verduin H and Dhont J K G 1995 *J. Colloid Interface Sci.* **172** 425
[20] Tanaka S, Ataka M and Ito K 2002 *Phys. Rev.* E **65** 051804
[21] Sedgwick H, Kroy K, Salonen A, Robertson M B, Egelhaaf S U and Poon W C K 2005 *Europhys. J.* E **16** 77
[22] Dinsmore A D and Weitz D A 2002 *J. Phys.: Condens. Matter* **14** 7581
[23] Poulin P, Bibette J and Weitz D A 1999 *Eur. Phys. J.* B **7** 277
[24] Bibette J, Mason T G, Gang H and Wietz D A 1992 *Phys. Rev. Lett.* **69** 981
[25] Dickinson E and Golding M 1997 *Food Hydrocolloids* **11** 13
[26] Bergenholtz J and Fuchs M 1999 *Phys. Rev.* E **59** 5706
[27] Kroy K, Cates M E and Poon W C K 2004 *Phys. Rev. Lett.* **92** 148302
[28] Sciortino F, Mossa S, Zaccarelli E and Tartaglia P 2004 *Phys. Rev. Lett.* **93** 055701
[29] Doi M and Edwards S F 1986 *The Theory of Polymer Dynamics* (Oxford: Clarendon)
[30] Tanaka H, Nishikawa Y and Koyama T 2005 *J. Phys.: Condens. Matter* **17** L143
[31] Tanaka H and Nishikawa Y 2005 *Phys. Rev. Lett.* **95** 078103
[32] Tanaka H, Araki T and Koyama T 2003 *J. Phys.: Condens. Matter* **15** S387
[33] Tanaka H and Araki T 2000 *Phys. Rev. Lett.* **85** 1338
[34] Araki T and Tanaka H 2005 *Phys. Rev.* E at press