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LETTER TO THE EDITOR

Network-forming phase separation of colloidal suspensions

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Abstract

Colloidal suspension can be regarded as an ideal model system of emulsions, protein solutions, foods, and inks. When there are strong attractive interactions between colloidal particles, they aggregate, phase separate, and sometimes form gel. The basic understanding of the resulting formation of superstructures is of crucial importance from both the scientific and industrial viewpoints. Here we provide clear experimental evidence suggesting that phase separation of colloidal suspensions can take the following kinetic pathway accompanying a metastable transient gel state: upon the phase separation, a percolated network is formed by a hierarchical clustering mechanism even at an extremely low colloid volume fraction ($<10^{-3}$). Then the network structure coarsens with time under the influence of the connectivity and the resulting self-generated mechanical stress. The similarity of this behaviour to droplet-forming viscoelastic phase separation in a dilute polymer solution suggests that colloid phase separation may be classified as viscoelastic phase separation.

 Supplementary data files are available from stacks.iop.org/JPhysCM/17/L143

Phase separation is one of the most fundamental phenomena responsible for the formation of heterogeneous structures in condensed matter [1, 2]. It is commonly observed in various kinds of condensed matter 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 convection driven by the motion of the interface. Contrary to this conventional wisdom on normal phase separation (NPS), we previously found a new type of phase separation in polymer solutions [3], which can be described by neither the solid nor the fluid model of phase separation. Near a critical composition, it is characterized by the appearance of a transient gel

in the initial stage of phase separation, the formation of a networklike structure of a polymer-rich phase, its break-up, and the resulting phase inversion. Unlike NPS, which produces only two kinds of phase-separation morphologies, droplet and bicontinuous structures, viscoelastic phase separation can transiently produce network (or sponge) structures. We called this new type of phase separation ‘viscoelastic phase separation (VPS)’ since viscoelastic effects, which are spontaneously produced by the dynamic crossover between the characteristic rate of deformation and that of viscoelastic relaxation, play key roles in phase separation in addition to diffusion and hydrodynamic effects. The appearance of a transient gel is the most characteristic feature of VPS in polymer solutions. ‘Dynamic asymmetry’ and the resulting ‘asymmetric stress division’ are the essential physical origins of VPS [4].

A colloidal suspension, which is a mixture of large particles and small liquid molecules, is another typical example of dynamically asymmetric mixtures. Thus, colloidal suspensions look similar to polymer solutions in the sense that both have intrinsic ‘dynamic asymmetry’ between their components, reflecting the size disparity. However, there is also a crucial difference between them: polymers have large internal degrees of freedom, while colloids 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 [5], but they do not exist in colloidal suspensions. These differences give us an impression that viscoelastic effects are not so important in phase separation of colloidal suspensions. So it is not clear whether phase separation of colloidal suspensions should be similar to that of classical fluid mixture (NPS) or to that of polymer solutions (VPS).

It is known [6] that addition of non-absorbing polymers to a colloidal suspension can cause phase separation: when colloids are close enough, there is an overlap of the depletion zones from which polymers are sterically excluded. The resulting unbalanced osmotic force causes attractive interactions between colloidal particles and leads to phase separation. For a deep quench, for example, the initial growth of concentration fluctuations is followed by the formation of a transient gel, and the coarsening process apparently stops for a while. This transient gel state lasts for a long time, and then the gel eventually collapses under gravity [7–11]. During this process, the apparent volume fraction of a colloid-rich (gel) phase decreases with time. Three-dimensional observations with laser-scanning microscopy also revealed that big holes are slowly created in a transient gel during the above process [10]. Its final state can be well described by the thermodynamic phase diagram. Similar transient gelation phenomena are also observed in phase separation of emulsions [12–14].

The importance of transient and permanent gelation in an attractive particle system and its relation to phase separation have also been studied theoretically and numerically for a long time [6, 15–21]. Their relevance has also been experimentally checked (see, e.g., [22]). Recently the mode-coupling theory has also been applied to describe the ergodic-to-nonergodic transition in attractive colloidal suspensions (see, e.g., [8, 23, 24] and the references therein). In relation to this, Sciortino *et al* [25] recently suggested that the formation of low density arrested states in a system where short-range attraction competes with long-range repulsion can be modelled as a glass transition, where clusters are trapped in cages generated by the long-range repulsion. Interplay between phase separation and slow dynamics associated with an underlying ergodic-to-nonergodic transition has attracted considerable interest. Although there have been many studies on this interesting subject, most studies have put the focus on geometrical percolation and the mode-coupling anomaly and the resulting slow dynamics. These concepts provide physical explanations for the slow dynamics. However, there have so far been few studies focusing on how the slow dynamics associated with these phenomena affects phase-separation kinetics *via their dynamic coupling*. For example, such slow dynamics

opens up the possibility that the deformation field created by phase separation can produce the mechanical stress fields in a transient gel, or in the interaction network of colloidal particles, even though individual particles cannot [20, 21]. This implies that phase separation of colloidal suspensions may be affected by viscoelastic effects. It is of conceptual importance for our understanding of phase separation and its kinetic pathway to reveal how the connectivity of a transient gel and the resulting self-generated mechanical stress affects phase separation of colloidal suspensions. It is the aim of this letter to experimentally clarify the basic nature of phase separation of colloidal suspensions, focusing on these points. We note that the origin of the mechanical stress (or the viscoelastic effects) is attractive interaction between particles, which is also the driving force of phase separation and gelation.

The system studied is an aqueous suspension of monodisperse charged colloids. We used fluorescent polystyrene latex particles (Polyscience, monodisperse polystyrene latex containing rhodamine, diameter = 50 nm) as charged colloids, with NaCl as a salt. For sedimentation experiments, we used only H₂O (no density match). At $t = 0$, we mixed colloids suspended in pure water with a salt solution in a sample tube and measured the height of the meniscus h as a function of time t . For microscopy observation, on the other hand, we matched the density of colloids (1.05 g cm^{-3}) with that of a salt solution by mixing H₂O (1.00 g cm^{-3}) with D₂O (1.10 g cm^{-3}) appropriately 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, with 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 $\sim 10 \text{ s}$, using the salt diffusion constant of $\sim 80 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. This is fast enough for studying the initial stage of phase separation. Phase separation in a colloidal suspension has so far been initiated by directly mixing it with either a polymer solution or a salt solution. 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 very 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 [6], the energy barrier for aggregation is estimated as $\sim 12k_B T$ for $\phi_s = 1.0 \text{ wt\%}$, $\sim 1k_B T$ for $\phi_s = 5.0 \text{ wt\%}$, and it disappears for the higher ϕ_s .

We observe the pattern evolution process with confocal fluorescent microscopy (Yokokawa Electric. Co., CSU21, excitation wavelength 532 nm), equipped with a high speed CCD camera (Nobby Tech. Ltd, Phantom V4.1). We control the confocal microscopy, the camera, the piezo-focusing system (Physik Instrum., E-662 LV), and the electric shutter (Newport Co., 846HP) in a coherent manner to obtain a 2D image (512×512) every 1 ms. With this system, we are able to capture a 3D image (a hundred 2D images: $409.6 \mu\text{m} \times 409.6 \mu\text{m} \times 80 \mu\text{m}$ with a resolution of $0.8 \mu\text{m}$) within 100 ms.

The structure factor $S(q)$ was obtained by averaging the power spectra of the two-dimensional Fourier transform for 2D slices along the z direction. The Euler characteristic χ_E was calculated from a digitized 3D image by using the following relation: $\chi_E = F + V - E$, where F , V , and E are the numbers of faces, vertices, and edges of all polygons, respectively [26, 27]. Note that $\chi_E = 2 - 2g$, where g is the genus of the surface (the number of handles in the structure). We define χ_E such that it is positive for isolated clusters while it is negative for network structures with many holes.

In our experiments, we controlled the interaction between colloids by adding salt. With an increase in the salt concentration ϕ_s , the electrostatic repulsion is screened more significantly

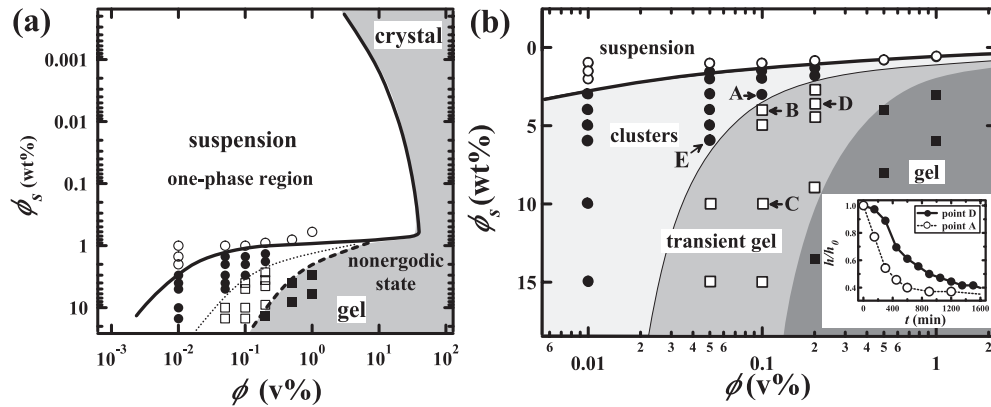


Figure 1. (a) Phase diagram of charged colloidal suspensions. The axis of ϕ_s is inverted to invoke the similarity to the T - ϕ phase diagram in protein solutions and the phase diagram of colloid-polymer mixtures, although this way of plotting is unconventional. Note that the amount of salt is somewhat equivalent to an energy or an inverse temperature $1/T$. The crystalline phase exists for a lower salinity, but crystallization is inhibited by gelation for a higher salinity ($\phi_s \geq 1$ wt%). In our experiments, crystallization was never observed for $\phi_s \geq 1$ wt% for a period of more than six months after phase separation. (b) Phase diagram of colloidal suspensions. The inset, which plots the scaled height h/h_0 (h_0 being the height at $t = 0$) against time t , shows the typical sedimentation behaviours observed in the cluster region (point A) and in the transient gel region (point D). The phase boundary is determined by the sedimentation kinetics in a macroscopic sample after mixing a salt-free colloidal suspension with a salt solution. In the suspension region (at the points indicated by open circles), a system is in a homogeneous liquid state and there is no sedimentation. In the cluster region (at the points indicated by closed circles), sedimentation starts immediately after the mixing without delay, as shown in the inset (point A). The phase separation accompanies the formation of isolated clusters, which is confirmed by 3D confocal microscopy observation. In the transient gel region (at the points indicated by open squares), the delayed sedimentation is observed, as shown in the inset (point D). The phase separation proceeds with the formation of networklike patterns, which is confirmed by 3D confocal microscopy. In the gel region (at the points indicated by closed squares), no sedimentation takes place (namely, $h/h_0 = 1$ for any t) since the gel is strong enough to support the gravitational force and thus it is permanent.

and thus the van der Waals attractive interactions start to prevail over repulsive interactions. For a given colloid volume fraction ϕ , thus, a system becomes unstable and starts to phase separate above a critical salt concentration. If the attractive interaction is strong enough and the volume fraction of colloids ϕ is high enough, a system enters into a transient gel state in the early stage of phase separation. For a higher salt concentration, a system even forms gel, which is not transient but practically permanent. For this case, thus, a system cannot reach the equilibrium state due to the nonergodic nature of the gel state. Although a crystalline phase should exist as an equilibrium phase for a high colloid volume fraction (see figure 1(a)), crystallization has never been observed for our samples since it is inhibited by gelation for a high salinity. Under gravity, these three states can be distinguished by observing the kinetics of sedimentation, which is a result of the competition between the gravitational stress and the yield stress of gel. For a case of usual phase separation, sedimentation immediately takes place just after mixing a colloidal suspension with a salt solution (see the inset (for point A) of figure 1(b)). For a case of transient gel formation, a space-spanning turbid transient gel is first formed, but after a certain latency period the fast sedimentation takes place; the clear zone of a dilute suspension (almost pure water) starts to be formed below the air-suspension interface and the sedimentation front falls gradually until the volume fraction of the colloid-rich phase reaches its final value. This process is characterized by the delay of the onset of the fast sedimentation (see the inset (for point D) of figure 1). Such delayed sedimentation was studied for colloid-polymer mixtures in

detail experimentally by Poon and co-workers [8] and theoretically by Evans and Starrs [21]. For a case of permanent gel formation, there is no sedimentation after the formation of a space-spanning turbid gel, and this gel state lasts for a long time: more than months.

By using the above three kinds of behaviours as fingerprints, we made a dynamic phase diagram of our system. The boundary between a transient gel regime and a permanent one depends upon how long we wait before the initiation of sedimentation. However, we confirmed that this dependence becomes very weak if the waiting time exceeds several days. Thus, we chose this characteristic waiting time as two weeks. For the gel state determined by this definition, we have confirmed that no sedimentation takes place at least for more than half a year. The dynamic phase diagram obtained in this way is shown in figure 1(b) as a function of the volume fraction of colloids, ϕ , and the salt concentration, ϕ_s . Our results show that a colloidal suspension can form a transient gel even at volume fraction less than 0.1 v%. This result can be explained by the following scenario: colloidal particles first form rather open clusters and these clusters further form a percolated structure. Here we point out that the percolation threshold may be strongly influenced by the kinetic factors, in particular, by long-range hydrodynamic interactions [28]. This hierarchical network formation can be the mechanism responsible for the formation of a transient gel at very low volume fractions of colloids, which may be generic to colloids, proteins, and polymers. The relevance of the above scenario of the cluster-to-network transformation is confirmed experimentally, as will be shown later (see figure 5).

To further elucidate the difference in the phase-separation dynamics between NPS and VPS, we directly observe the pattern evolution process during colloidal phase separation induced by the osmotic injection of salt with 3D confocal microscopy and we studied the elementary coarsening processes of phase separation. The behaviours observed at points A and C are summarized as follows. At point A, where normal sedimentation without delay is observed, we confirm that NPS occurs (see figure 2(a)). Just after the osmotic injection of salt, colloidal particles start to aggregate or phase separate. Then droplets of a high colloid particle density are formed and their size gradually grows, primarily due to the Brownian-coagulation mechanism, which is confirmed by real-time 2D observation and by the coarsening behaviour (see figure 4(a)). We confirm that the total number of clusters N decreases with time as $N \propto t^{-1}$, which is typical of the domain coarsening due to the Brownian-coagulation mechanism (see figure 4(a)). At point C, where transient gel formation is confirmed in the macroscopic observation of sedimentation, we find that the phase-separation behaviour is essentially different from that observed at point A, as anticipated from the macroscopic observation. Instead of droplet phase separation, clusters form a transient gel with a fine network structure soon after the injection of salt (see figure 2(b)). The backbones of the network are fluctuating thermally, but they are stretched mechanically by the force created by interparticle attractions and eventually break up one by one. We have confirmed by real-time 2D microscopic observation that the backbones are stretched during the reorganization of the network structure. The existence of the mechanical stress is further confirmed by the following fact: a transient gel is sometimes peeled off from the wall by accompanying the mechanical fracture, if the adhesion of particles to the glass wall is not strong enough to support the mechanical stress accumulated in the network. This leads to the rapid collapse of the transient gel. This crucial dependence of the behaviour on the boundary condition is one of the most significant characteristics of VPS [4]. The shape of the colloid-rich domain is not controlled by the interfacial tension, but by the elastic force balance condition¹. Thus, the elementary process

¹ In relation to this, we point out that since a network pattern produced by VPS automatically satisfies the elastic force balance condition, we can say that it is a mechanically optimized structure.

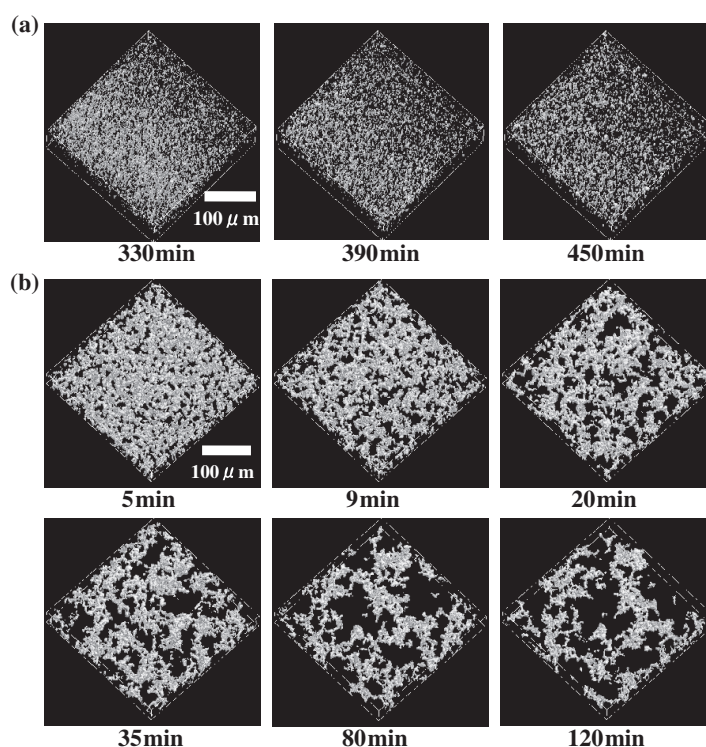


Figure 2. Temporal change in 3D phase-separation patterns ($240 \mu\text{m} \times 240 \mu\text{m} \times 80 \mu\text{m}$ with $0.8 \mu\text{m}$ resolution) during phase separation observed at point A (a) and point C (b). Note that the structural coarsening is much faster in (b) than in (a).

of coarsening may be the stress concentration on a weak point of the network, its resulting break-up, and the mechanical relaxation to a new metastable configuration (see below for the mechanism). We also estimate the volume fraction of the colloid-rich phase as ~ 0.1 . For NPS, the phase-separated structure should have droplet morphology for this volume fraction [1, 2]. All these facts are suggestive that colloidal phase separation may be VPS, and not NPS.

This coarsening of the network is quite surprising in the following sense: aggregation of aqueous particles is typically thought to occur when the repulsive barrier is removed by adding salt and so they fall into a deep primary minimum. If less salt is added, then there is a delay in the aggregation, but when it does occur it again results from the particles falling into the same deep minimum. If this is the case, particles are not thought to be able to rearrange themselves. Coarsening after aggregation implies absolutely that there is mass transfer of the particles within the clusters.

Let us discuss the mechanism of the breakage of the network. Although the adhesive energy must be quite strong, the stress concentration into the deformable weak part of the backbones can lower the energy barrier for the bond breakage [4]. If we neglect the effects of the stress concentration, thermal activation is the only process of structural arrangements. For this case, the rate-limiting process for breakage of a backbone is the thermal activation of a few load-bearing particles, of radius a , out of several attractive potentials of bond energy U_0 . Given that z is the number of bonds required to be broken in order for a load-bearing particle to hop (or rotate) from its site on a backbone to a neighbouring site, and a small number of such

rearrangements cause a backbone to yield, dissipating its stored elastic energy, the average lifetime of a backbone, of a fractal dimension d_f , is [19, 21]

$$\tau_b \sim \left(\frac{\xi}{2a}\right)^{-d_f} \left(\frac{\Delta^2}{D_0}\right) \frac{\exp(z\beta U_0)}{(z\beta U_0)^2}, \quad (1)$$

where $\beta = 1/k_B T$ (k_B : Boltzmann constant), ξ is the characteristic cluster size, D_0 is the diffusion constant of a particle, Δ is the range of the interaction potential. The factor $N_b = (\xi/2a)^{d_f}$ is the number of sites at which the backbone could yield. For $\beta U \sim 20$, for example, τ_b is extremely long and we cannot expect the breakage of the network. This gives us an impression that the network may be permanent and should not coarsen with time for this case. 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 (δx), $(1/2)k\delta x^2$, where k is the elastic constant [4]. Thus U_0 in the above expression should be replaced by $U_0 - (1/2)k\delta x^2$ under the action of the stress. This stress is generated to reduce the total interfacial energy, which 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. This can happen even for large U_0 . Note that the larger adhesive energy means a larger interfacial energy and thus a larger elastic energy. This mechanism leads to successive breakage of the stress-bearing backbone as long as the self-generated stress is strong enough to break up the backbone. We emphasize that the coarsening (of a network) is driven by the interfacial energy in VPS as in NPS. Since the slow mechanical relaxation under stress may be called viscoelastic behaviour, we may classify this phase separation as VPS [20].

Our classification of colloid phase separation as VPS is further supported by comparison of network-forming phase separation in colloidal suspensions with VPS observed in dilute polymer solutions. In a concentrated polymer solution, a network structure of the polymer-rich phase is directly formed from a transient gel similarly to the volume shrinking transition of a chemical gel [4]. In a very dilute polymer solution, on the other hand, droplets of polymer-rich phase are first formed and then they form a network structure [29] despite the polymer-rich phase being a minority phase. Since the polymer-rich phase first forms droplets, the process of the phase separation after droplet formation is strikingly similar to that of colloid phase separation, as shown in figure 3. The unique common feature of these phase-separation behaviours is that the network structure of the slower-component-rich phase is formed despite it being a minority phase. We stress that this morphological feature cannot be explained by means of the conventional knowledge of NPS. Because of the experimental difficulty in making a very thin cell for osmotic injection, experiments in a quasi-two-dimensional (2D) situation are difficult for colloidal suspensions.

For polymer solutions, on the other hand, we can directly observe the process of VPS in a quasi-2D cell in real time. In the video (see the Supplementary Information available at stacks.iop.org/JPhysCM/17/L143), we show the phase-separation process of a mixture of polystyrene (the weight-averaged molecular weight: 2.06×10^7 ; the polydispersity ratio: 1.1) and diethylmalonate (0.3 wt% polystyrene). The sample was quenched to $T = 25.0^\circ\text{C}$, which is 4.9 K below the binodal line. One side of the image corresponds to $74.3 \mu\text{m}$. The total time of the video corresponds to 320 s. There we can see the elementary process of network coarsening in a dilute polymer solution, which clearly shows the role of the mechanical stress in the network coarsening. We believe that this behaviour may be essentially the same as that of colloidal suspensions, since for both cases the network is formed by attracting particles.

Let us analyse the coarsening behaviour more quantitatively. Figure 4(a) shows the temporal change in the number of droplets N for phase separation for $\phi = 0.05$ v% and

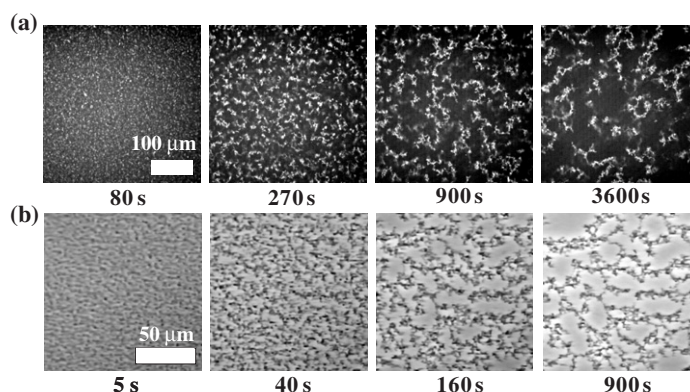


Figure 3. Comparison of pattern evolution observed in a colloidal suspension (a) and that in a polymer solution (b). (a) is observed in a colloidal suspension ($\phi = 0.25$ v%, $\phi_s = 15$ wt%) with 2D confocal microscopy, while (b) is observed in a mixture of polystyrene (its weight-averaged molecular weight being 706 000) and diethyl malonate (0.5 wt% polystyrene) at $T = -20$ °C with phase-contrast microscopy. A sample was confined in a thin glass cell with a thickness of $10 \mu\text{m}$. The temperature was controlled within ± 0.1 K by a computer-controlled hot stage (Linkam LK-600PH) with a cooling unit (Linkam L-600A). Note that in (a) the colloid-rich phase has bright contrast, while in (b) the polymer-rich phase has dark contrast. Network patterns observed in a colloidal suspension are strikingly similar to those in a dilute polymer solution, which are produced by VPS (see also the video in the Supplementary Information at stacks.iop.org/JPhysCM/17/L143). For both cases, the backbones of the network are mechanically stretched, although they have some fractal-like fine structures. This suggests that the network-forming phase separation observed in colloidal suspensions should be classified as VPS and that VPS may be universal for all dynamic asymmetric mixtures.

$\phi_s = 6$ wt% (at point E in figure 1(b)). N decays as $N \sim t^{-1}$, which is consistent with the Smoluchowski or Binder–Stauffer mechanism [1, 2] of NPS. This implies that this phase separation is basically the same as fluid phase separation or typical cluster aggregation. Figure 4(b), on the other hand, shows the temporal change in the structure factor $S(q)$ and the characteristic wavenumber q_p for the case of figure 2(b). The distinct peak in $S(q)$ means that there is a strong spatial correlation in the distribution of colloidal particles, which is characteristic of the ordering of a system of conserved order parameter. q_p decreases with time, indicating the coarsening of the network structure (see also figures 2(b) and 5). The time exponent for q_p is determined as about 0.5: $q_p \sim t^{-1/2}$. Since there is no self-similarity in the pattern evolution, however, this power-law behaviour might not have a significant meaning. Note that this coarsening law is not consistent with any laws known for NPS: $q_p \propto t^{-1}$ for hydrodynamic coarsening of bicontinuous phase separation while $q_p \propto t^{-1/3}$ for droplet phase separation [1, 4].

Next we extract the topological characteristics of the phase-separation structure [26, 27]. The results of topological analysis are shown in figure 5 for pattern evolution observed at points A, B, and C in the phase diagram of figure 1. The Euler characteristic χ_E is substantially negative for case C, which indicates that the structure is a network having many holes in it. The decrease of $|\chi_E|$ with time means a decrease in the number of holes in the network structure, which clearly indicates the coarsening of the network structure. Interestingly, χ_E becomes negative only after a long incubation time for case B, which indicates the topological transformation from clusters to a percolated network. This supports the scenario of the hierarchical network formation (see the small figure in figure 5); first isolated clusters formed by diffusion-limited aggregation and then they hierarchically formed a percolated network with the help of hydrodynamic interactions [28].

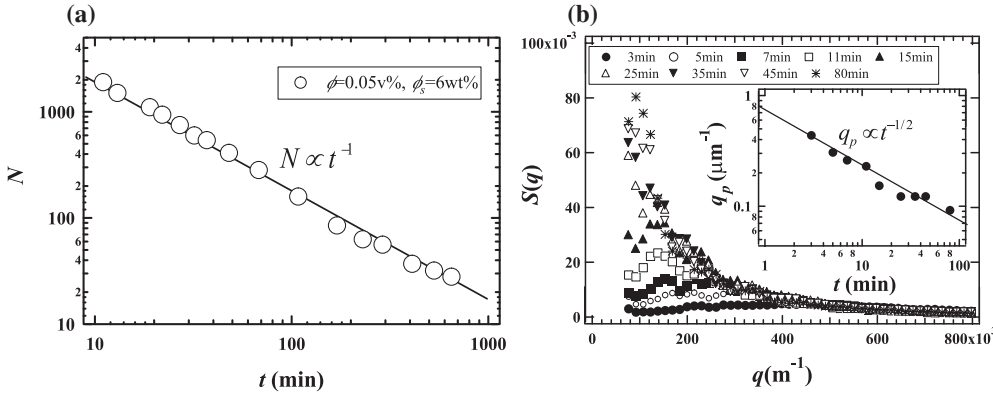


Figure 4. (a) Temporal change in the number of droplets N for phase separation for $\phi = 0.05$ v% and $\phi_s = 6$ wt% (at point E in figure 1(b)). The droplet number density decays as $N \propto t^{-1}$ as in NPS. (b) Temporal change in the structure factor $S(q)$ and the characteristic wavenumber q_p (inset) for phase separation at point C in the phase diagram of figure 1 (corresponding to figure 3(b)). The peak wavenumber coarsens with time as $q_p \propto t^{-1/2}$, differently from usual spinodal decomposition.

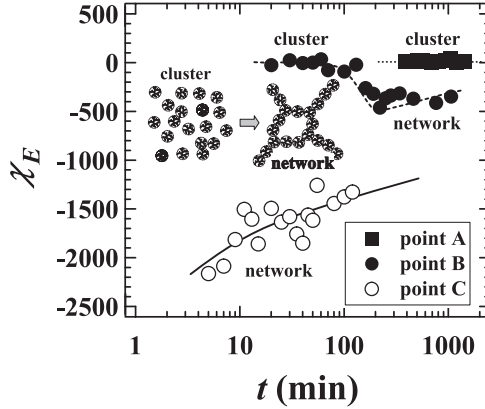


Figure 5. Temporal change in the Euler characteristics χ_E during phase separation of colloidal suspensions ($\phi_v = 1$ v%) observed at points A, B, and C of the phase diagram in figure 1. Here χ_E is calculated only for the domains whose volume is larger than 1000 times a lattice volume. At point A ($\phi_s = 3$ wt%), only isolated clusters are formed. The reason that χ_E is almost zero for this case is simply because we neglected small clusters whose volume is less than 1000 times a lattice volume. By counting all clusters, we confirm that positive χ_E slowly decreases and approaches 1 with time, reflecting the Brownian-coagulation mechanism. At point B ($\phi_s = 4$ wt%), the isotropic suspension initially forms clusters; then, around $t = 150$ min, these clusters form the percolated network structure due to attractive interactions between them, with the help of hydrodynamic interactions [28], in a hierarchical manner, which makes χ_E largely negative. This scenario naturally explains why a transient gel can be formed even at extremely low volume fractions of colloids. At point C ($\phi_s = 11$ wt%), the network is formed even in the very early stage and thus χ_E is largely negative. This suggests that the time of cluster-to-network transformation, t_{c-n} , becomes shorter with increasing ϕ_s .

In summary, we have experimentally found that a colloidal suspension forming a transient gel upon its phase separation forms a percolated network structure, which coarsens with time under the influence of the self-generated mechanical stress. This coarsening process is reminiscent of VPS. The similarity of this behaviour to droplet-forming VPS in a dilute polymer

solution suggests that colloidal phase separation may be classified as VPS². This implies that transient gelation is a kinetic pathway characteristic of viscoelastic phase separation. Our study suggests that strong dynamic asymmetry (or size disparity) between the components of a mixture may be the only necessary condition for transient gel formation and thus for VPS. We emphasize that the viscoelastic nature of the component of a mixture itself is not necessary for the occurrence of VPS; the viscoelastic nature of the phase separation stems from the viscoelastic properties of a transient gel (or interaction network) itself, namely, the slow mechanical relaxation under stress. This suggests that VPS may be *universally* observed in any mixtures having dynamic asymmetry between the components, which includes most of the complex fluids such as polymer solutions, colloidal suspensions, emulsions, and protein solutions³. This may have a considerable impact on our understanding of how network structures are formed in nature, particularly, in soft matter and biomatter. The connection of our approach to the percolation concept and the mode-coupling theory via the relevant constitutive relation remains a problem for future investigation.

Finally, our study suggests that Nature does not necessarily take a kinetic pathway, which reduces the free energy of a system in a simple manner, and the formation of a transient gel brings a system to an unexpected kinetic pathway. In this kinetic path, the connectivity between the slow components forming a transient gel prevents the system from undergoing phase separation via diffusion, but instead induces *phase separation via mechanical fracture*. This further implies that the classification of the kinetics of phase separation into nucleation growth type and spinodal decomposition type, which is performed by analysing the thermodynamic stability of the system on the basis of the free energy, cannot be straightforwardly applied for network-forming phase separation of colloidal suspensions; the kinetic pathway is determined not only by the thermodynamic factors, but also by the kinetic (mechanical) factors.

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² It should be noted that the network structure may be permanent rather than transient in our system if there are no gravitational effects.

³ Our study may also provide us with clues for clarifying the relationship among aggregation, phase separation, and gelation, which we believe are generic to these dynamically asymmetric mixtures.

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