

Spontaneous coarsening of a colloidal network driven by self-generated mechanical stress

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Abstract – Colloidal suspensions can be regarded as an ideal model system for such key daily materials as emulsions, protein solutions, foods, and inks. When colloidal particles strongly attract each other, they aggregate, phase-separate, and sometimes form gels. The basic understanding of this spatially heterogeneous jamming process is of crucial importance from both scientific and industrial viewpoints. Usually it is believed that if colloids attract very strongly with adhesion energy more than 10 times the thermal energy, networks formed by aggregation do not coarsen with time and a stable gel is immediately formed. Contrary to this common belief, we demonstrate by numerical simulation that the coarsening of a colloidal network can proceed by self-generated mechanical stress even without any thermal noise for a system of long-range interactions: fracture-induced coarsening. This remarkable kinetic pathway of purely mechanical origin may shed new light on our basic understanding of the stability and aging (or coarsening) behaviour of colloidal gels.

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Understanding the slow dynamics of glassy soft matter is a major challenge of condensed matter physics [1]. The stability of colloidal suspensions, protein solutions, and emulsions also plays a crucial role in physical, chemical, and life science, and also in cosmetics, ink, detergent, paint, and food industries [2–12]. Attractive interactions between particles are the common driving force of crystallization, phase separation, aggregation, and gelation. When these phenomena occur at the same time, they can dynamically couple. Colloidal suspensions behave as fluid when particles are homogeneously suspended in a solvent, but they often behave as nonergodic solids upon colloidal instability. The formation of a percolated network structure of colloids upon aggregation is the cause of this jamming phenomenon known as gelation and the resulting drastic change in the mechanical properties. This state is characterized by its unique combination of mechanical (stress-bearing) and transport properties, which are useful in materials science.

It may be worth noting here that gelation is specific to a mixture whose components have large “size (or dynamic) asymmetry”. Colloidal suspensions, protein solutions, and

polymer solutions all belong to this category of dynamically asymmetric mixtures [13–16]. For example, because colloids are much larger than the surrounding liquid molecules, they move much more slowly, this dynamic asymmetry means the fast molecules can relax on timescales many orders of magnitudes faster than slow, large particles. We stress that this dynamic asymmetry is a key to gelation.

Gelation shares many common features with other ergodic-to-nonergodic transitions such as liquid-glass transition. This generality is also applied for the aging behaviour [3,4,17]. Aging represents irreversible slow time evolution of disordered solids, which is a manifestation of breakdown of time-translational invariance [18]. Such behaviour is common to spin glasses, electron glasses, vortex glasses, structural glasses, and gels. Universal features of the aging of these systems including glassy soft matter have recently attracted a considerable attention [2–4,17–19]. Among these, however, a gel is characterized by its spatially heterogeneous arrested structure, which is often caused by a competition between phase separation and jamming [1,15,17]. Recently, the ergodic-to-nonergodic transition in attractive colloidal suspensions has been approached with mode-coupling theory to draw a unified picture of jamming phenomena

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in both repulsive and attractive systems (see, *e.g.*, [2–4,8,20,21] and references therein). Roles of geometrical and energetic constraints and the resulting mode-coupling anomaly in the slow dynamics have been demonstrated. However, there have been only a few studies focusing on roles of self-generated mechanical stress on the coarsening of a colloidal network [4,15,17,22,23]. We have recently found the coarsening of network for colloidal suspensions, where colloids attract very strongly with adhesion energy more than 10 times the thermal energy [12]. This phenomena may not be explained by conventional non-destructive mechanisms based on the thermal activation process. Here we demonstrate a novel “fracture-induced” coarsening mechanism of purely mechanical origin, employing a numerical simulation.

Numerical studies of colloidal aggregation and phase separation have so far been made mainly by using Brownian dynamics simulations [24–27], where the hydrodynamics is free draining. The most difficult problem in simulating colloidal suspensions arises from many-body hydrodynamic interactions between solid particles [6]. There are several useful methods to overcome this difficulty (see [28,29] and references therein). Here we employ the “Fluid-Particle Dynamics (FPD)” method [30]: In this method we treat a colloidal particle as an undeformable, but very viscous fluid particle, instead of treating particles as solid particles.

Here we briefly explain our FPD simulation method [30]. A particle whose centre of mass is located at \mathbf{r}_i is represented by a “smooth” viscosity change as $\eta(\mathbf{r}) = \eta_s + \sum_i^N (\eta_c - \eta_s) \phi_i(\mathbf{r})$, where η_s is the liquid viscosity and η_c is the viscosity inside a colloid particle. The summation is taken over all the particles (N particles). ϕ_i represents a particle i as $\phi_i(\mathbf{r}) = \{\tanh((a - |\mathbf{r} - \mathbf{r}_i|)/\xi) + 1\}/2$, where a is the radius of a particle and ξ is the interface thickness. The equation of motion is then given by

$$\rho \frac{\partial}{\partial t} \mathbf{v} = \mathbf{F} - \nabla p + \nabla \cdot [\{\eta(\nabla \mathbf{v} + (\nabla \mathbf{v})^t)\} + \boldsymbol{\sigma}^R], \quad (1)$$

where ρ is the density, and \mathbf{F} is the force field. $\boldsymbol{\sigma}^R$ is the thermal stress noise, which satisfies $\langle \sigma_{ij}^R(\mathbf{r}, t) \sigma_{mn}^R(\mathbf{r}', t') \rangle = 2k_B T \eta(\mathbf{r}) \{(\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm}) \delta_{mn}\} \delta^3(\mathbf{r} - \mathbf{r}') \delta(t - t')$. Here pressure p is determined to satisfy the incompressible condition $\nabla \cdot \mathbf{v} = 0$. As an interparticle potential for our simulations, we used a Lennard-Jones potential $U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where ϵ is the strength of the potential and σ is the range of interaction. Although this potential is not typical for colloids, we use it to see the effects in a clearer manner. The relevance of such long-range attractions in colloidal suspensions and protein solutions was discussed, *e.g.*, in [25,31]. The averaged potential energy per particle $\langle U \rangle$ is calculated as $\langle U \rangle = \frac{1}{N} \sum_{i \neq j} \sum_j U(|\mathbf{r}_j - \mathbf{r}_i|)$. We define $a_{LJ} = 2^{7/6} a$ (note that we set $\sigma = 2a$). We also made simulations using the Asakura-Oosawa (AO) potential [5], which is more relevant to a colloid-polymer mixture (see below). \mathbf{F} is determined by the above

interparticle potential as $\mathbf{F}(\mathbf{r}) = \sum_i^N \phi_i(\mathbf{r}) \sum_j^N \mathbf{f}_{ji}$, where $\mathbf{f}_{ji} = -(\partial/\partial \mathbf{r}_i)U(|\mathbf{r}_j - \mathbf{r}_i|)$ is the force acting on particle i , which interacts with particle j . Initially particles are distributed randomly in space while avoiding the overlap between them. Then we solve the above equation by the Marker-and-Cell (MAC) method with a staggered lattice under the periodic boundary condition. Under the force field \mathbf{F} determined by the particle distribution, we calculate the steady velocity field by using eq. (1). By calculating the average velocity of each particle $\mathbf{v}_i = \int d\mathbf{r} \mathbf{v}(\mathbf{r}) \phi_i(\mathbf{r}) / \int d\mathbf{r} \phi_i(\mathbf{r})$, we move particles by $\Delta \mathbf{r}_i = \mathbf{v}_i \Delta t$, where Δt is a time step. Then we map all the particles, which are treated off the lattice, on the lattice and we repeat the above procedure with a new particle distribution. In this way, we can simulate the phase-separation dynamics of colloidal suspensions while including interparticle hydrodynamic interactions. The larger is η_c/η_s , the better the approximation. The simulations contain $N = 1600$ particles in a two-dimensional (2D) square cell ($L^2 = 512^2$) and $N = 729$ ones in a three-dimensional (3D) cubic cell ($L^3 = 100^3$). The particle size was $a = 3.6$ in 2D and $a = 3.2$ in 3D simulations. The volume fraction ϕ was 0.249 and 0.100 in 2D and 3D, respectively. The other parameters were $\xi = 1$, $\epsilon = 0.25$, $\eta_s = 0.5$, $\eta_c = 25$, $\rho = 1$, and $\Delta t = 0.01$ in both simulations.

First we show the aggregation process of colloidal suspensions simulated by the above method in figs. 1(a) and (b), respectively, for 2D and 3D. In (b), the pattern is coarse-grained to make the 3D structure more visible by replacing ϕ_i with a Gaussian field $\psi_i(\mathbf{r}) = \exp(-|\mathbf{r} - \mathbf{r}_i|^2/\xi^2)$. The coarse-grained network structure shown in the figure is described by the isosurface of $\sum_i \psi_i(\mathbf{r})$. We calculate the stress tensor acting on particle i as $\mathbf{P}_i = \sum_j (\mathbf{r}_j - \mathbf{r}_i) : \mathbf{f}_{ji}$, where $:$ is the diad operator. The trace of \mathbf{P}_i is then calculated as $p_i = \sum_j (\mathbf{r}_j - \mathbf{r}_i) \cdot \mathbf{f}_{ji}$. The value of p_i is expressed by the colour in fig. 1. Red and blue colour mean a negative and positive pressure (or, stretching and compression force) acting on a particle, respectively. In (a), a particle with more reddish colour is in a higher energy state; namely, the system is locally stretched there, so the interparticle distance from that particle to its neighbours is longer compared to the equilibrium case. Colour in (b) has the same meaning as in (a). Randomly distributed colloidal particles form a percolated (interaction) network soon after the initiation of phase separation. This network formation is promoted by hydrodynamic interactions [30]. This effect is more pronounced in 2D, but plays an important role also in 3D. Without hydrodynamic interactions, particles have a tendency to aggregate and form a compact structure or at most a thick network structure [30], as is often seen in Brownian dynamics simulations [24–27]. After the formation of a transient gel, particles tend to increase the number of nearest neighbours so as to reduce the interaction energy. For the network to thicken, however, some stretched parts of the network must be broken up.

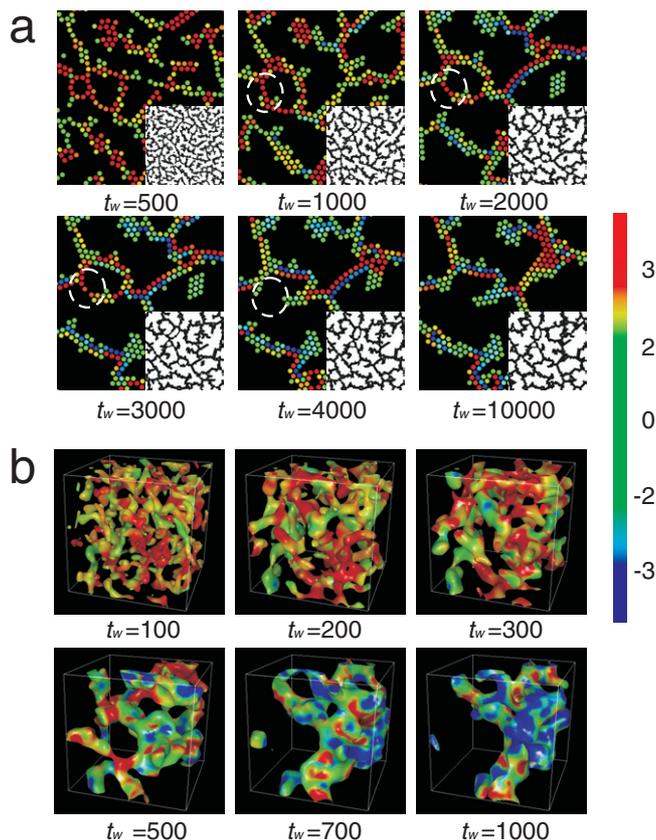


Fig. 1: (Colour on-line) Phase-separation process in colloidal suspensions. (a) 2D pattern evolution. The insets show the evolution of the overall structure, whereas the figures show a part of it with the stored stress, which is expressed by the colour of each particle (see text). (b) 3D pattern evolution (see the text on the details).

From the colour of particles, we can clearly see that the stress is concentrated selectively on the thin (weak) stretched parts, which are in a high-energy state (red). This stress concentration eventually leads to the breakup of such parts. In this way, the network structure relaxes into a lower metastable energy state (blue). For further relaxation, this process must be repeated. This is the elementary process of coarsening of the interaction network. In both 2D and 3D, the fraction of the reddish (high energy) particles having less neighbours decreases with time, indicating the gradual transformation from an open network to a more compact structure, which leads to the reduction of the total free energy. Inclusion of the thermal stress noise σ_{ij}^R does not alter the basic behaviour. With weak stress noise, a network structure temporally fluctuates while keeping the force balance condition. At a junction point of the network, three and four arms tend to be connected to satisfy the local force balance condition, respectively, for 2D and 3D. Hereafter we discuss the characteristics of network coarsening (or, aging), using the results of 2D simulation since for 3D simulation the separation between the characteristic size

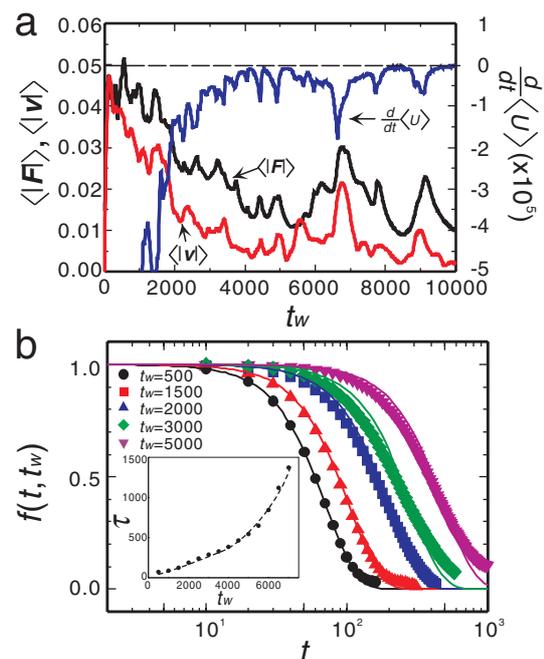


Fig. 2: (Colour on-line) Kinetics of stress-induced coarsening in 2D. (a) Temporal change in the rate of the change in the average potential energy per particle $\langle U \rangle$, $\frac{d}{dt}\langle U \rangle$, the magnitude of the average fluid velocity $\langle |v| \rangle$, and the average strength of the self-generated force per particle, $\langle |\mathbf{F}| \rangle$. (b) Aging process of the self-intermediate scattering function, $f(t, t_w)$. The solid lines are the fitted function (see text). The inset shows the t_w -dependence of τ . The dashed line is an eye guide.

of the network and the size of the simulation box is not sufficiently large for detailed analysis.

To see the discrete nature of the elementary coarsening mechanism, we show in fig. 2(a) the temporal change in the rate of the change of the averaged potential energy per particle $\langle U \rangle$, $\frac{d}{dt}\langle U \rangle$, the magnitude of the average velocity field $\langle |v| \rangle$, and the average mechanical force $\langle |\mathbf{F}| \rangle$ ($= \sum_i \sum_j |\mathbf{f}_{ji}|/N$). We note that the total energy monotonically decreases with time ($\frac{d}{dt}\langle U \rangle \leq 0$), as expected. The spikes in the curves correspond to the breakup events of the network, where the strength of the velocity field abruptly increases. Before this abrupt increase in the velocity fields, the stress increases gradually and relaxes after the breakup of the network. The strong correlation among $\frac{d}{dt}\langle U \rangle$, $\langle |\mathbf{F}| \rangle$, and $\langle |v| \rangle$ clearly tells us that the stress concentration and the resulting breakup of the network cause the abrupt change in these quantities. The strongly intermittent nature may be a unique feature of stress-driven aging. For a finite system, the decrease in the energy occurs in a discrete way, reflecting the discrete nature of the elementary process of bond breakage. This is characteristic of “intermittent network fracture”.

This slow structural relaxation may be regarded as “aging” [2–4], since the system is a disordered solid with finite elasticity. Here we show the temporal

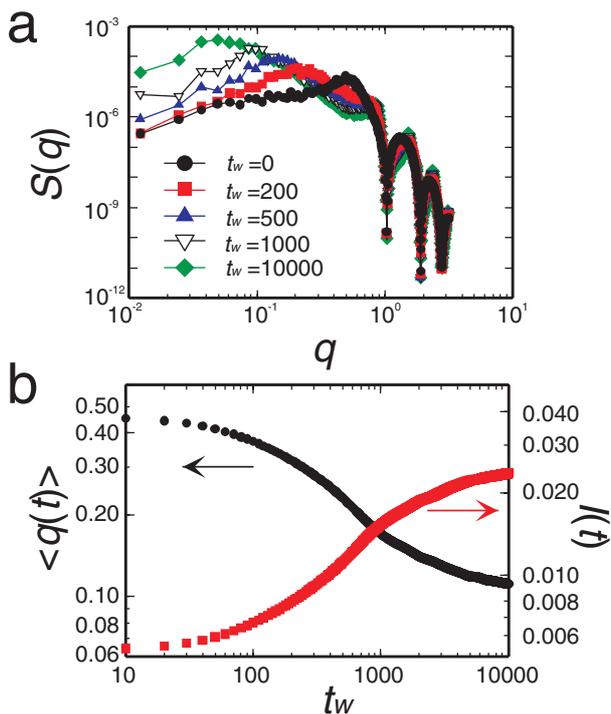


Fig. 3: (Colour on-line) Averaged coarsening kinetics of colloidal network. (a) Temporal change in the structure factor $S(q)$. (b) Temporal change in the characteristic wave number $\langle q \rangle$ and the peak intensity I .

change in the self-intermediate scattering function of particle motions, $f(t, t_w)$ (t_w being the waiting time), in fig. 2(b). $f(t, t_w)$ is calculated as $f(t, t_w) = 1/(N_p t_s) \sum_j \int_{t_w}^{t_w+t_s} dt' e^{i\mathbf{q} \cdot \{\mathbf{r}_j(t'+t) - \mathbf{r}_j(t')\}}$, where \mathbf{q} is the wave vector. The wave number $q = |\mathbf{q}|$ is fixed at $q = 2\pi/a_{LJ}$. t_s is the sampling time and we employed $t_s \cong 2\tau$. $f(t, t_w)$ is well described by $f(t, t_w) = \exp\{-(t/\tau)^2\}$ (solid lines), which is characteristic of force-driven particle motion. This reflects the (ballistic) motion of particles driven by mechanical force [4,15,17,22]. This Gaussian decay is reasonable for our case, where there is no thermal diffusion. This can be regarded as an extreme case of compressed exponential decay [4,22]. The slowing-down of the dynamics with aging, *i.e.*, the increase in the relaxation time τ with t_w , can clearly be seen (see the inset of fig. 2(b)). Here τ is obtained by the above fitting. Such nearly exponential growth of τ as a function of t_w was also seen in experiments [4,17], which might be characteristic of stress-driven aging.

Next we characterize the slow time evolution of the network structure. Figures 3(a) and (b) show the temporal change in the structure factor $S(q)$ and the characteristic wave number of the structure factor $\langle q \rangle$. $S(q)$ is calculated by using 2D Fourier transformation as $S(q) = \frac{1}{2\pi q \Delta q} \int_{q \leq |\mathbf{q}'| \leq q + \Delta q} d\mathbf{q}' \langle \tilde{\phi}(\mathbf{q}') \tilde{\phi}(-\mathbf{q}') \rangle$, where $\Delta q = 2\pi/L$ and $\tilde{\phi}(\mathbf{q})$ is the Fourier transform

of $\phi(\mathbf{r})$. The characteristic wave number is then calculated as $\langle q \rangle = \int dq q S(q) / \int dq S(q)$. Multiple peaks in a high-wave-number region of $S(q)$ reflect the form factor of an individual particle. After the initial linear regime [32], where $\langle q \rangle \sim t_w^0$, the characteristic wave number decreases with time, apparently obeying the following power law in the (rather narrow) intermediate regime: $\langle q \rangle \sim t_w^{-1/2}$.

Our simulations clearly indicate that it is “interparticle attraction” that is the common origin of both osmotic and mechanical stress: The former is a driving force of phase separation (or aggregation), while the latter tends to prevent it mechanically. The breakup of the interaction network is driven by the thermodynamic driving force, but the connectivity of the network tends to prevent it. Once the network structure, *i.e.*, a transient gel, is formed, the breakup of energetic bonds between particles is inevitably required for increasing the number of nearest neighbours and lowering the free energy of a system (fig. 2). Thus, the system has to overcome the energetic barrier associated with this breakup of bonds. In the above we demonstrated that this can be achieved not only thermally, but also mechanically. The occurrence of the network coarsening even in a simulation without any thermal noise unambiguously indicates that the self-generated stress can break up the network.

Now we discuss this novel mechanism of the breakage of the network in more detail. Although the adhesive energy ϵ must be strong ($\epsilon/k_B T = \infty$, where k_B is Boltzmann constant, in our simulation at $T = 0$), the stress concentration into the deformable weak part of the backbones can lower the energy barrier for the bond breakage. If we neglect the effects of the stress concentration, the 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 ϵ . 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 estimated as [23,27]

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

where $\beta = 1/k_B T$, l is the characteristic cluster size, D_0 is the diffusion constant of a particle, Δ is the range of the interaction potential. The factor $N_b = (l/2a)^{d_f}$ is the number of sites at which the backbone could yield. Without thermal noise, τ_b is infinite, which means that the network is permanent and should never coarsen with time. However, our simulation results tell us that the action of mechanical stress entirely changes the situation. The effective potential can be lowered by the elastic energy stored by the deformation of the backbone (δx), $(1/2)k_0 \delta x^2$,

where k_0 is the elastic constant at the potential minimum ($k_0 = \partial^2 U / \partial r^2$ at $r = a_{LJ}$). Thus ϵ in the above expression should be replaced by $\epsilon - (1/2)k\delta x^2$ under the action of the stress. This stress is generated to reduce the attractive interaction energy among many particles. 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 irrespective of the value of $\epsilon/k_B T$ (even without any thermal noise, or at $T = 0$!, which is the case here). Usually it is believed that particles attracted by strong adhesion energy more than ten times the thermal energy are essentially permanently connected. Contrary to this common belief, however, our mechanism can lead to successive breakage of the stress-bearing backbone as far as the self-generated stress is strong enough to break up the backbone, which is the case for a system of long-range interactions. Here long-range interactions mean that the range of interaction is long enough for a system to feel a way of particle motion leading to the reduction of the interaction energy in a deterministic manner. The opposite case is that the reduction of the energy is made solely by random thermal motion.

The above argument holds for a harmonic potential of depth ϵ . For a real potential, which is generally unharmonic as in the LJ potential employed here, the mechanical instability of a stretched force chain occurs for a negative spring constant, *i.e.*, for $k(r) = \partial^2 U / \partial r^2 \times a_{LJ}^2 / \epsilon \leq 0$ ($r = |\mathbf{r}_j - \mathbf{r}_i|$), even in the absence of thermal activation: For a spring with zero or negative k , there is no restoring force. To confirm this, we studied the temporal change in the distribution of the local spring constant k at various stretching levels under the self-generated stress. The result is shown in fig. 4(a). The absence of the particles having largely negative k supports our physical picture. Note that for $k < 0$ (in the yellow region) a bond becomes intrinsically unstable under stretching and it must break up. The light blue region, where $k > k(r = a_{LJ})$, on the other hand, corresponds to compressed particle pairs by interparticle attractive interactions. With an increase in time, the number of relaxed bonds increases. On the other hand, the number of highly stretched bonds, h , which is going to be broken up or under the process of debonding, decreases, as shown in fig. 4(b). We may say that if h becomes negligibly small, the coarsening of the network stops and the network almost becomes permanent: gelation. Thus, this monotonic decay of h may be an indication of a transition from a transient to a permanent gel. This is consistent with the fact that the coarsening tends to slow down in the late stage (see fig. 3(b)), which is suggestive of such a transition. In some cases (not shown), h even increases with time. For such cases $\langle U \rangle$ rapidly decays with time and the coarsening also proceeds smoothly.

Next we show the distribution function of the interparticle force f_b , $p_f(f_b)$, in fig. 4(c). Here $f_b = -\partial U / \partial r \times a_{LJ} / \epsilon = -\mathbf{f}_{ij} \cdot \mathbf{r}_{ij} / |r_{ij}|$, and f_b has the minimum value at $r_c = (13/7)^{1/6} a_{LJ}$. Particle pairs of $r > 13^{1/6} a_{LJ}$, at which

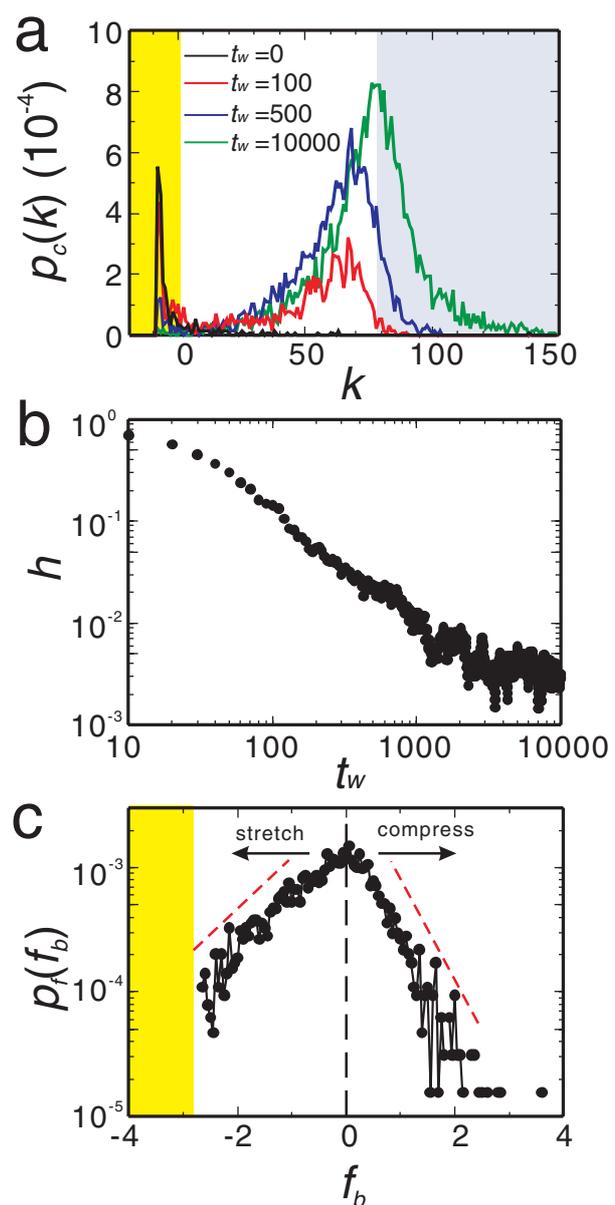


Fig. 4: (Colour on-line) Temporal change in the population of highly stretched bonds in the network and the force distribution. (a) The distribution function of k , $p_c(k)$, for particle pairs. (b) Temporal change of the number of particles having negative k in the yellow region (particles under the process of debonding), h . (c) The force distribution function $p_f(f_b)$ at $t_w = 1000$.

k becomes minimum, are neglected. $p_f(f_b)$ roughly obeys $p_f \sim \exp(-|f_b|/g_b^\pm)$ for both compressing and stretching forces, although the decay rate g_b^\pm is different between them. Such exponential distribution for compression forces is often observed in jamming systems [33]. The unique feature arises from the existence of the inaccessible force region (the yellow region in fig. 4(c)) for the stretching side. This is because a bond must be broken above r_c due to the loss of its restoring ability. It is also a characteristic feature of mechanically-driven coarsening.

Finally, we note the relative importance of this mechanism of mechanical origin to the mechanism of thermal activation. We performed simulations of colloids interacting with AO potential $U_{AO}(r)$ [5], which is relevant to a binary colloid mixture. We employed the potential, whose derivative is given as $U'_{AO} = c\{(D+d)^2 - D^2\}$ for $r < D$, $U'_{AO} = c\{(D+d)^2 - r^2\}$ for $D < r < D+d$, and $U'_{AO} = 0$ for $D+d < r$. Here D represents a particle diameter, which is set as $D = a_{LJ}$, and $c = \epsilon/(d^2D + 2d^3/3)$, where ϵ and $d = RD$ give the depth and range of the potential. R is a non-dimensional parameter characterizing the range of the potential relative to the particle size. We also introduce a soft core potential, which prevents the overlap of particles, as $U_{sc}(r) = \epsilon(2a/r)^{12}$. The other simulation procedures are exactly the same as in the LJ case. Although the results are not shown, we find that our mechanism is more important for longer-range interactions, as expected. For $R > 0.5$, we see the similar coarsening behaviour. For smaller R (particularly, less than 0.2), thermal noise is essential for the coarsening, but even for this case mechanical stress plays some roles in the breakup of network and the resulting coarsening. This problem will be discussed in detail elsewhere.

In sum, we reveal a novel mechanism of the coarsening of a network structure, of purely mechanical origin, which is essentially different from the widely known coarsening mechanism due to thermal activation. This mechanism is particularly important for particles interacting with rather long-range (relative to particle size) attractions. We show that the coarsening of a gel can proceed by fracture of a percolated network by self-generated mechanical stress. The jammed state of particles with attractive interactions can be destabilized purely mechanically even without thermal noise, contrary to the intuition that any nonergodic state should be stable at zero temperature. This can be regarded as spontaneous stress aging at zero temperature. This finding may deepen our basic understanding of the stability and aging of a gel state, which is an important nonergodic state of soft and biomatter. Experimental verification of this mechanism by measuring force acting on a network, *e.g.*, using elastooptic effects of colloids made of gel balls or optical tweezers, are highly desirable.

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