

## How Things Get Stuck: Kinetics, Elastohydrodynamics, and Soft Adhesion

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(Received 13 December 2011; revised manuscript received 7 February 2012; published 30 May 2012)

We consider the sticking of a fluid-immersed colloidal particle with a substrate coated by polymeric tethers, a model for soft, wet adhesion in many natural and artificial systems. Our theory accounts for the kinetics of binding, the elasticity of the tethers, and the hydrodynamics of fluid drainage between the colloid and the substrate, characterized by three dimensionless parameters: the ratio of the viscous drainage time to the kinetics of binding, the ratio of elastic to thermal energies, and the size of the particle relative to the height of the polymer brush. For typical experimental parameters and discrete families of tethers, we find that adhesion proceeds via punctuated steps, where rapid transitions to increasingly bound states are separated by slow aging transients, consistent with recent observations. Our results also suggest that the bound particle is susceptible to fluctuation-driven instabilities parallel to the substrate.

DOI: 10.1103/PhysRevLett.108.226104

PACS numbers: 68.35.Np, 81.40.Pq, 87.17.Rt

The dynamics of interfacial attachment in a fluid medium, mediated by specific adhesive bonds, is of interest and applicability to several physical and biological systems. Although details regarding the microscopic structure of tethers, distribution of attachment sites, and geometry of the substrates do vary greatly, the essential physics involved is common to various phenomena including the coagulation of subunits in biochemical processes [1], binding using DNA covered nanoparticles [2], aging of a stuck colloid [3], tethering and adhesion of cells [4–8], and the capture efficiency of immersed, sticky surfaces [9]. In these scenarios, substrates come into close proximity, allowing the longest polymeric tethers to provide the initial attachment between substrates. This initial attachment draws the two substrates closer, draining the intervening fluid out and allowing shorter polymeric tethers to themselves provide further attachment. Here we explore this generic attachment process as a function of the basic geometric, structural, and kinetic parameters governing the process.

A minimal model of the phenomena may be idealized in terms of a fluid-immersed spherical particle of radius  $a$  that can stick to a flat, rigid substrate grafted with adherent elastic binders, illustrated in Fig. 1(a). The fluid is assumed to have a viscosity  $\mu$ , density  $\rho$ , and temperature  $\theta$ , with the particle at a distance  $[a + h_0(t)]$  from the rigid substrate, as shown in Fig. 1(b). The adherent binders are idealized as polymers with one end attached to the substrate and the other capped by a sticky head of radius  $a_b$ . We model each binder as a linear Hookean spring of stiffness  $\mathcal{K}_s$  and mean rest length  $\ell$  [10,11]. When subject to thermal fluctuations, the binder heads may eventually contact the particle and stick (here we assume that the reaction is diffusion limited), exerting an elastic force on the particle. If binding events are rare and the mean rest lengths of

tethers are well spaced, then the particle may move towards the substrate in a stepwise manner, where long intervals with relatively little motion are punctuated by short bursts of transitions to more bound states closer to the substrate; indeed, this phenomenology of punctuated aging is suggested by recent experiments [3].

Owing to the large aspect ratio of the gap between the colloid and the substrate, the viscous drag on the sphere is dominated by lubrication forces and is greater than the viscous drag on the adhesive molecule provided  $a/h_0 \sim 10^2 \gg 1$  and  $a/a_b \sim 10^4 \gg 1$ , respectively, as suggested by using typical values from the cited literature. Additionally, this disparity in sizes allows us to neglect the thermal agitation of the particle while retaining the fluctuations in the binder lengths. In the limit where the areal density of bonds,  $n_0$ , is low (typical values being  $n_0 \ell^2 \sim 10^{-9} \ll 1$ ), the attached binders do not impede the flow of fluid [12–14].

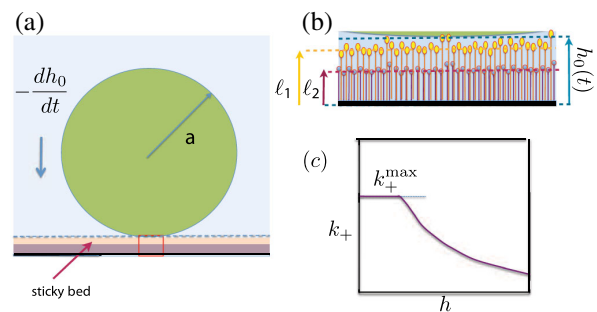


FIG. 1 (color online). (a),(b) Schematic of the system: The center of the particle of radius  $a$  lies a distance  $a + h_0(t)$  above a substrate. The close-up on the right shows a two-family system, with the rest lengths  $\ell_1$  and  $\ell_2$ . (c) The binding affinity of a tether,  $k_+$ , follows from a Kramer's analysis, saturating when binding events are very likely.

Two additional simplifications allow us to focus on the dynamics normal to the substrate and ignore tangential displacements of the settling sphere. First, we neglect the effect of the shear flow on the mean rest length of the adhesive bonds. Second, we neglect the shearing effect of the mean flow on the binders, thus causing them to bind at an angle to the vertical. This is reasonable provided the torque due to thermal fluctuations dominates the torque on the binder due to the streaming flow. For the shearing flow to have negligible effect on the statistical properties of the bonds, we require  $\dot{\gamma}\mu\ell/\kappa \ll 1$  with  $\kappa$  being the characteristic stiffness (a mean field value) of the bonds and  $\dot{\gamma}$  being a mean shear rate. Here we assume that the rest length of the tethers is not modified by the flow and, vice versa, that the flow is not modified by the tethers.

Since the motion of the particle towards the substrate drives the fluid out of the intervening gap, the effect of inertia is quantified via the Reynolds number based on the gap size  $\text{Re}_{h_0} \equiv \mu(dh_0/dt)(h_0/a)^2 a/\rho \ll 1$ . The effect of inertia at the colloid scale  $\text{Re} \equiv \mu(dh_0/dt)a/\rho$  is also typically less than unity. For a neutrally buoyant colloidal particle at height

$$h(t) = h_0(t) + a(1 - \sqrt{1 - r^2/a^2}) \quad (1)$$

( $r$  being the radial coordinate) above a substrate that is decorated with Hookean tethers (spring constant  $K_s$ ) parametrized by their rest length  $\ell$  and number density  $n(\ell, t)$ , the equation of motion is

$$\frac{6\pi\mu a^2}{h_0} \frac{dh_0}{dt} + 2\pi\mathcal{K}_s \int_{\ell} d\ell \int_0^a n(r, \ell, t)(h - \ell)rdr = 0. \quad (2)$$

Here the first term in Eq. (2) is the leading order force on the sphere that models the increasing difficulty in draining fluid out of the gap as  $h_0 \rightarrow 0$  [15], while the second term characterizes the elastic forces on the colloid due to the bound tethers [10,11]. In many biological systems, the distribution of lengths of the tethers is bimodal [11], and so here we study a two-family system of binders for which

$$n(\ell, t) = n_1(t)\delta(\ell - \ell_1) + n_2(t)\delta(\ell - \ell_2), \quad (3)$$

$n_i(t)$  being the areal density of bound bonds of the  $i$ th family attached at a height  $h$  at time  $t$  and  $\delta(s)$  is the Dirac delta function. To close Eqs. (1)–(3), we need to specify equations for the binder dynamics. Assuming first-order kinetics for the attachment and detachment process [10,11,16], we write

$$\frac{dn_i}{dt} = k_{\text{on}}(n_{i,0} - n_i) - k_{\text{off}}n_i, \quad (4)$$

where  $n_{i,0}$  ( $i = 1, 2$ ) is the total area density (attached plus detached) of bonds,  $k_{\text{on}}$  is the attachment rate, and  $k_{\text{off}}$  is the detachment rate. Given some initial conditions,

Eqs. (1)–(5) constitute a set of coupled, nonlinear equations for the height  $h$  as a function of  $n_1$  and  $n_2$ .

Since the particle is being drawn closer to the substrate rather than being pulled away [11,17], we choose the off rate to be a constant and explore the consequences of a displacement dependent attachment rate. Provided the settling rate is slow, one may assume that binders attach at a rate that depends solely on the distance the heads have to traverse in order to stick to the particle. In this limit,  $k_{\text{on}}$  depends on the extension  $h(t) - \ell$ . By adopting a Kramers-style argument [16,18], in the limit of large extension  $h \gg \ell + (2k_B\theta/\mathcal{K}_s)^{1/2}$  the asymptotic approximation to the mean first passage time and thus  $k_{\text{on}}$  yields (Supplemental Material, Sect. I [19])

$$k_{\text{on}} \approx D_b\sqrt{2}(h - \ell)\left(\frac{\mathcal{K}_s}{k_B\theta}\right)^{3/2} e^{-(\mathcal{K}_s/2k_B\theta)(h-\ell)^2}, \quad (5)$$

$D_b$  being the diffusion constant of the binder head. For small extensions, the asymptotic expression (5) is not valid. We note that the maximum value  $k_{\text{on}}^{\text{max}}$  is attained at  $h = \ell + (k_B\theta/\mathcal{K}_s)^{1/2}$ . To obtain a tractable, continuous expression, we set  $k_{\text{on}} = k_{\text{on}}^{\text{max}}$  for  $h \leq \ell + (k_B\theta/\mathcal{K}_s)^{1/2}$ .

Typical values for parameters appearing in Eqs. (1)–(5) are  $a \approx 10^{-6}$  m,  $\mu \approx 10^{-2}$  Pa s,  $n_0 \approx (10^7\text{--}10^9)$  m $^{-2}$ ,  $a_b \approx 10^{-10}$  m,  $\ell \approx 10^{-8}$  m, and  $\mathcal{K}_s \approx (0.01\text{--}10) \times 10^{-3}$  N m $^{-1}$ . To make sense of these values, we introduce the dimensionless variables  $H \equiv h/\ell_1$ ,  $R \equiv r/a$ ,  $T \equiv tk_{\text{on}}^{\text{max}}$ ,  $\mathcal{L}_i \equiv \ell_i/\ell_1$ , and  $N_i \equiv n_i/n_{i,0}$ . Then, Eqs. (1)–(5) can be written as the following dimensionless versions:

$$\frac{\alpha}{H_0} \frac{dH_0}{dT} = \int_0^1 [N_1(1 - H) + N_2(\mathcal{L}_2 - H)]RdR, \quad (6)$$

$$H(R, T) = H_0(T) + q(1 - \sqrt{1 - R^2}), \quad (7)$$

and

$$\frac{dN_i}{dT} = K_{\text{on}}^{(i)}(R)(1 - N_i) - K_{\text{off}}N_i \quad (i = 1, 2), \quad (8)$$

where the attachment rate constants in dimensionless variables are  $K_{\text{on}}^{(i)} = 1$  for  $H \leq (\frac{1}{2\beta})^{1/2} + \mathcal{L}_i$  and  $K_{\text{on}}^{(i)} = [2\beta(H - \mathcal{L}_i)^2]^{1/2} e^{-\beta(H - \mathcal{L}_i)^2}$  for  $H > (\frac{1}{2\beta})^{1/2} + \mathcal{L}_i$ . Three important dimensionless parameters appear in Eqs. (6)–(8): The parameter  $q \equiv a/\ell_1$  (typical values  $\approx 10^2 \gg 1$ ) characterizes the finite curvature of the particle, and the parameter  $\beta \equiv (\frac{1}{2}\mathcal{K}_s\ell_1^2)/k_B\theta$  controls the attachment rate and is the thermal energy, while the parameter  $\alpha \equiv 3\mu(n_{1,0}\mathcal{K}_s\ell_1)^{-1}(k_{\text{on}}^{\text{max}})$  contrasts the viscous time  $\mu/(n_{1,0}\mathcal{K}_s\ell_1)$  and the chemical limiting binding time  $(k_{\text{on}}^{\text{max}})^{-1}$ . Of special relevance is the limit  $\alpha \gg 1$ , which corresponds to a system where the rate limiting step is the time for viscous drainage of the fluid from between the particle and the substrate. Finally,  $\rho \equiv n_{2,0}/n_{1,0}$  is the ratio of the number density of total bonds of the two families and thus a measure of the contrast in grafting densities.

The sticking process is initiated with the base of the sphere at the rest height of the longest tethers chosen here to be family 1, i.e.,  $H(0) = 1$ , with no initial bonds, so that  $N_1(0) = N_2(0) = 0$ . We start with a consideration of the case of a single family of irreversible bonds so that  $N_2(R, T) = 0$  and  $K_{\text{off}} = 0$ . Then, solving the system (6)–(8) numerically shows that the kinetics of particle capture has two regimes—a rapid settling regime (I) followed by a much slower aging regime (II) as shown in Fig. 2(a). In the settling regime, bonds attach over a characteristic region and the colloid descends rapidly towards the surface. This phase terminates at a height when central tensile forces, which push the sphere away from the substrate, balance the dominant peripheral compressive forces over a region with vertical extent  $\beta^{-(1/2)}$ . A scaling estimate of this height gives  $(1 - H_0^*) \sim \beta^{-(1/2)}$ . The characteristic region of adhesion over which the initial binding occurs is  $R^* \sim q^{-(1/2)}\beta^{-(1/4)}$  (Supplemental Material, Sect. II [19]). Within this region, all bonds are in their bound state. Outside this region, bonds attach very slowly—a larger fraction binding as time increases. The region of adhesion grows very slowly, as the bonds need to make very long excursions compared to their rest length to be able to stick to the particle, and the balance between

the attractive forces due to slowly attaching bonds and viscous resistance to fluid drainage determines the settling speed (regime II). We find that the initial stages of regime II may be described analytically (Supplemental Material, Sect. II [19]). Past the initial rapid descent, the sphere begins to descend slowly with the sphere height decaying as

$$H_0 \approx H_0^* \exp(-t/\tau_{\text{aging}}), \quad \text{with } \tau_{\text{aging}} \sim q\alpha\beta \quad (9)$$

setting the characteristic time scale of the aging phase. This scaling for the decay rate is valid so long as the radius of adhesion is less than  $\sqrt{H_0/q}$ . The ultimate dynamics once binders attach at  $R \gg \sqrt{H_0/q}$  is, however, even slower than the above equation suggests (Supplemental Material, Sect. II [19]), and the sphere makes physical contact with the substrate only as  $T \rightarrow \infty$  due to the divergence of the viscous drag term. In the final state, the binders exert a net positive force pushing the sphere towards the surface, and hence energy has to be expended in order to dislodge the sphere. This final bound state can be understood as the end result of a series of differential stages. At each stage of the descent, additional bonds must attach to the periphery (at increasingly larger  $R$ ) and then draw the colloid closer to the substrate below until the elastic forces are in approximate balance with the adhesion radius attaining a certain value. The sphere waits (albeit, momentarily) and then executes the next stage once bonds attach again beyond the adhesion region established previously.

The settling scenario changes quite dramatically if one allows for even a small detachment rate. In Fig. 2(b), we show that the tail of the bound tether distribution now has a cutoff at  $H = H_{\text{cutoff}}$  determined by the detachment rate  $K_{\text{on}}^{(1)} \approx e^{-\beta(H_{\text{cutoff}}-1)^2} = K_{\text{off}}$ , thereby modifying the equilibrium height to a nonzero offset that is  $O(\sqrt{|\ln K_{\text{off}}|})$  provided that  $q \gg 1$ . In the absence of any other influences, contact between the particle and substrate is avoided, and the particle settles down as a nonzero height.

Inclusion of additional families of tethers with different equilibrium height distributions leads to a series of punctuated regimes of adhesion. In each regime, the slow aging process at the previous level results in the colloid being brought into reach of the shorter families of tethers. Their binding results in the rapid motion of the colloid before slowing and a subsequent repeat of the same process. Figures 3(a)–3(c) display the effect of having a second family of bonds with  $\ell_2 < \ell_1$  with the bonds attaching irreversibly. Four distinct regimes are seen—the first corresponds to the initial settling regime for the single family case; the second is the aging dynamics associated with the first family, drawing it towards the substrate slowly. When  $H_0 \sim \ell_2 + 1/\sqrt{2\beta}$ , a strong transition in the particle position is seen—evidenced by the knee in Fig. 3(a) at a time  $T \approx T^*$ . An increasing number of shorter bonds from the second family bind onto the particle, and

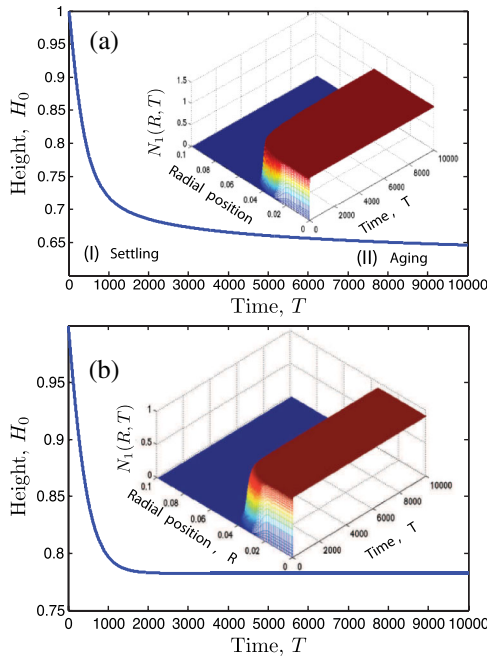


FIG. 2 (color online). The height of the particle,  $H_0$ , as a function of time  $T$  for a one-family binder system with  $N_{2,0} = 0$ ,  $\alpha = 100$ ,  $\beta = 100$ ,  $q = 500$ , and  $H_0(T = 0) = 1$ . (a)  $K_{\text{off}} = 0$ : An initial steep descent to a critical height is followed by a slow aging process with  $H_{\text{eq}}$  decaying exponentially to 0. (b)  $K_{\text{off}} \neq 0$ : Unlike in (a), the region of adhesion is bounded and the particle settles to a nonzero equilibrium height. The insets show the evolution of attached bond density when there is no unbinding and where there is some unbinding.

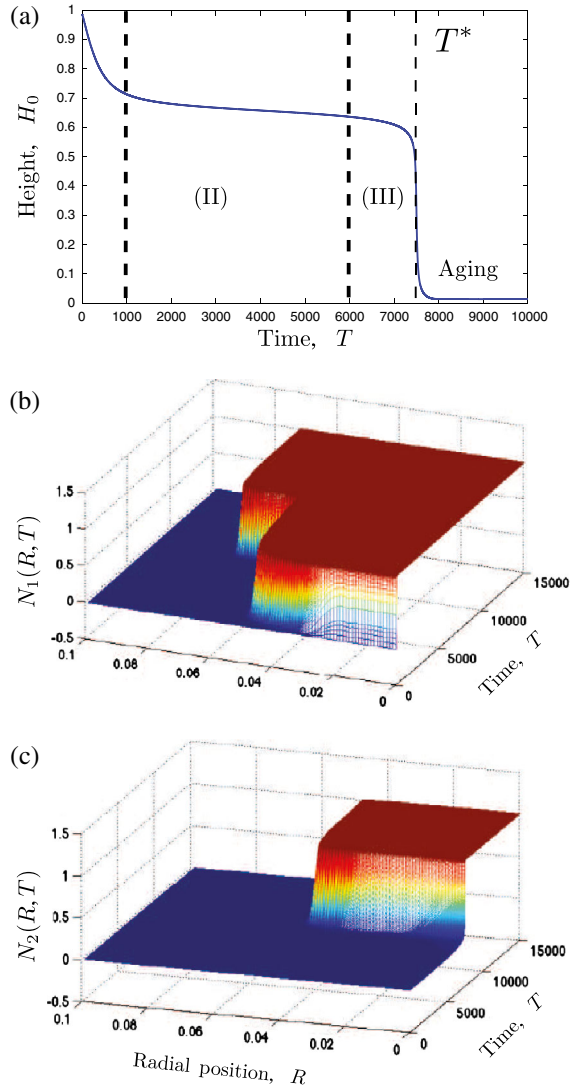


FIG. 3 (color online). Adhesion dynamics due to a two-family system for parameters  $N_{2,0}/N_{1,0} = 100$ ,  $K_{\text{off}} = 0$ ,  $\alpha = 100$ ,  $\beta = 100$ ,  $\mathcal{L}_2 = 0.25$ , and  $q = 500$ . (a) Height  $H_0$  versus time  $T$ . (b),(c)  $N_1$  and  $N_2$  as a function of radial distance from origin,  $R$ , and time  $T$ , respectively.

the exponentially slow decay transitions to a more rapid descent. An estimate of the time interval  $T^*$  may be obtained when the expression for the settling rate—Eq. (9)—is valid long enough for the particle to descend to a height  $H \approx \mathcal{L}_2 + 1/\sqrt{\beta}$ , when the second set of adhesive bonds start to bind. The time  $T^*$  is then given by (Supplemental Material, Sect. II [19])

$$T^* \sim q\alpha\beta \left| \ln \frac{\mathcal{L}_2 + 1/\sqrt{2\beta}}{H_0^*} \right|. \quad (10)$$

Our analysis has led to a simple picture for the kinetics of adhesion as limited by the dynamics of fluid drainage between the particle and the substrate. Our simple model for adhesive capture relates microscopic features such as

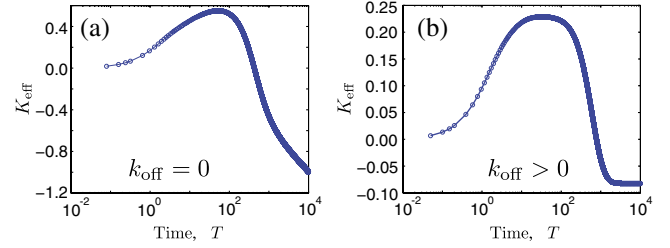


FIG. 4 (color online). The transverse linear elastic compliance  $K_{\text{eff}}$  due to the linear elasticity of attached binders for (a)  $k_{\text{off}} = 0$  and (b)  $k_{\text{off}} > 0$ . As the sphere settles, the sign of the resultant elastic force changes. Parameter values are the same as in Fig. 2.

kinetics and elasticity of individual adhesive bonds to macroscopically measured settling rates and aging times. We observe punctuated motion of the particle towards the substrate, which is an outcome of rare binding events. Such a punctuated aging process has been recently observed and been hypothesized to reflect a small number of metastable minima accessible to the system during attachment [3] in agreement with our interpretation. Although the punctuated aging process investigated here is due to families of binders with distinct rest lengths, similar effects would follow if the tethers were nonlinearly elastic. Additional effects due to steric hindrance and hydrodynamic or electrostatics effects on tether motions may also alter the dynamics [12,13], but we expect the gross features of the process to be preserved nonetheless.

We conclude with a brief discussion of the elastic response of the adhesively bound particle that stores elastic energy in the bonds which are compressed at the point of closest approach and extended away from it. This nonuniformity should lead to a nontrivial transverse linear compliance of the adhered particle when the sphere is subject to small amplitude, high frequency transverse displacements (Supplemental Material, Sect. III [19]). As the particle ages, it is unstable to small transverse displacements, whence the effective linear elastic compliance of the system,  $K_{\text{eff}} \sim 2\pi \sum_i \int_0^a \mathcal{K}_{s,n_i}(r,t) \left(\frac{h-\ell_i}{h}\right) r dr$ , is seen to change sign and become negative as the sphere gets closer to the substrate, as shown in Fig. 4 for both the case when the binders may detach or not. The physical mechanism underlying this linear instability is that attached binders near the center line are compressed while those attached far away are extended, so that the particle can move sideways and eventually has a soft mode associated with movement in a circle around the energetic minimum due to a competition between tether shear and compression. Incorporation of higher order terms and allowing bonds to attach at an angle to the vertical regularize this behavior. A careful experimental test of our theory is an obvious next step.

Funding for this research was provided by NIH via Grant No. 1R21HL091331-02 and the MacArthur Foundation (L.M.).

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# Supplementary Material for

## How things get stuck: kinetics, elasto-hydrodynamics and soft adhesion

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### I. CALCULATION OF THE FIRST PASSAGE TIME

Consider the motion of the binder (bond) head in a parabolic energy potential well where the energy  $U(x)$  is a function of the reaction co-ordinate,  $x$  - in this case the (vertical) extension relative to the rest length  $\ell$ . We choose to measure energies relative to  $x = 0$  so that  $U(0) = 0$ . When the binder reaches a height  $x_0$  such that  $U(x_0) = U_0$ , the well terminates - this point corresponds to the binder head attaching to the sphere. For attachment on the spherical colloid at a height  $h(t)$ , we require  $x_0 = h - \ell$ . A thermally agitated, unbound bond in such an environment will spend most of its time inside the well and primarily close to the minimum. Every now and then however, it might acquire a large enough kick due to random noise that enables it to scale the barrier. The flux or current of bonds that escape the barrier is thus related to the first passage time for escape.

To calculate this flux, we use two simplifications. We first posit that the binders do not spend time in reorientations required to attach when at the surface i.e, they attach immediately when encountering the surface. Thus the time needed for the chemical bond to form with the surface is assumed to be very small compared to the diffusive time scale of the head. The situation in our case is additionally complicated by the fact that the surface of the colloid is not stationary but is in motion. Close to the rigid substrate the particle settles slowly and its velocity  $\dot{h}_0$  is small relative to the rapidly fluctuating velocity of the unbound binder heads. The diffusion of the colloid is itself quite small compared to that of the much smaller binder heads. In this scenario, we can assume that the sphere descends negligibly in the time it takes for the binder heads to fluctuate appreciably. Using these two approximations, the escape flux may be used to obtain the attachment rate  $k_{\text{on}}$  for a binder to attach on the sphere at radial position  $r$ .

To obtain an analytical expression for the rate we calculate the steady solution to the Fokker-Planck equation governing the probability of finding a single binder with extension  $x_0$ . The binder

heads are restricted to move vertically and in this distinguished single dimension, the appropriate Fokker-Planck equation for the probability of finding a binder with extension  $x$  is

$$\frac{\partial P}{\partial t} = D_b \frac{\partial^2 P}{\partial x^2} - \frac{\partial}{\partial x} \left( \frac{F(x)}{\eta} P \right).$$

Here resistivity,  $\eta$ , arises due to the interaction of the binder molecule with the viscous surrounding fluid.  $D_b$  is the diffusion constant associated with a single adhesive binder molecule - in our case the binder head - of radius  $a_b$  in the ambient fluid at a given temperature. Since  $a_b \ll \ell$ , we ignore the change in the resistivity due to the presence of the wall. Finally, the binder head is assumed to move in a parabolic potential that exerts a force  $F$  of the form

$$F = -\frac{\partial U}{\partial x} = -\mathcal{K}_s x.$$

Here  $\mathcal{K}$  is the stiffness in the linear limit valid for Hookean springs.

Consider now the steady solution to the Fokker-Planck equation that satisfies the boundary conditions

$$P(x = x_0) = 0, \quad \text{and} \quad \frac{\partial P}{\partial x}(x = x_0) = j_0.$$

Integrating once and using normalization factors we obtain an expression for the escape flux,  $j_0$  as a function of  $x_0$ :

$$\frac{1}{j_0(x_0)} = \frac{1}{D_b} \int_0^{x_0} \exp\left(\frac{-\mathcal{K}_s x_1^2}{2k_B\theta}\right) dx_1 \int_y^{x_0} \exp\left(\frac{\mathcal{K}_s x_2^2}{2k_B\theta}\right) dx_2.$$

Considering large extensions  $\frac{1}{2}\mathcal{K}_s x_0^2 \gg k_B\theta$  allows us to localize the integrals and evaluate them asymptotically. The inner integral gets its dominant contribution from the region around  $x_0$  while the outer integral is mainly derived from evaluating around 0. The inner integral may be estimated as

$$\begin{aligned} \int_y^{x_0} \exp\left(\frac{\mathcal{K}_s x_2^2}{2k_B\theta}\right) dx_2 &\sim \int_{-\infty}^0 \exp\left(\frac{\mathcal{K}_s(x_0 + q)^2}{2k_B\theta}\right) dq \\ &\sim \frac{k_B\theta}{\mathcal{K}_s x_0} \exp\left(\frac{\mathcal{K}_s x_0^2}{2k_B\theta}\right). \end{aligned}$$

The outer integral is approximately

$$\int_0^{x_0} \exp\left(\frac{\mathcal{K}_s y^2}{2k_B\theta}\right) dy \approx \left(\frac{k_B\theta}{2\mathcal{K}_s}\right)^{\frac{1}{2}}.$$

Combining these expressions, we obtain the dimensional form of equation (5) of the main text

$$\frac{1}{j_0(x_0)} \approx \frac{1}{D_b} \left(\frac{k_B\theta}{2\mathcal{K}_s}\right)^{\frac{1}{2}} \left(\frac{k_B\theta}{\mathcal{K}_s x_0}\right) \exp\left(\frac{\mathcal{K}_s x_0^2}{2k_B\theta}\right)$$

## II. ESTIMATES OF THE REGION OF ADHESION, $R_c$ AND TRANSITION-TIME, $T^*$ .

The end of the settling phase in figure (2a) occurs when the majority of forces in the system are balanced and enough time has not elapsed for bonds to start attaching outside the near-contact region. Attached bonds are extended differently according to the value of  $R$ , thus exerting a different force on the sphere. It is clear that bonds within  $R = 1$  are compressed while bonds at the periphery beyond the radius of adhesion,  $R_c$ , are extended. Said more quantitatively, there is a narrow region,  $1 < R < R_c$ , where bonds attach efficiently with  $K_{on} = 1$ . The dimensionless expression for  $K_{on}$  makes clear that the vertical extent of this region is  $1/\sqrt{2\beta}$ , which naturally defines  $R_c$  according to

$$1 + \frac{1}{\sqrt{2\beta}} = H_0 + \frac{qR_c^2}{2}. \quad (\text{SI-1})$$

obtained using the paraboloid approximation to the sphere surface. This yields one relationship between  $H_0$  and  $R_c$ . A second relationship follows from the approximate force balance between the compressed and extended bonds

$$\int_0^1 (1 - H) N_1 R dR \approx \int_0^{R_c} (1 - H) R dR = 0. \quad (\text{SI-2})$$

Note that within  $R < R_c$  all bonds are bound,  $N_1 = 1$ . Combining the two equations above yields approximate expressions for the height at which the rapid descent ends and the extent of adhesion,

$$(1 - H_{0,c}) \sim \beta^{-1/2}, \quad \text{and} \quad R_c \sim q^{-1/2} \beta^{-1/4}. \quad (\text{SI-3})$$

Said another way, were the attachment rate a simple step function,  $K_{on} = 1$  for  $H \leq \left(\frac{1}{2\beta}\right)^{\frac{1}{2}} + 1$  and  $K_{on} = 0$  for  $H > \left(\frac{1}{2\beta}\right)^{\frac{1}{2}} + 1$ , then  $H_{0,c}$  would be the rest height of the particle. The settling phase is defined as the phase during which the particle settles to this new height,  $H_{0,c}$ .



The question that follows is of course what happens after this initial settling phase? Consider the dimensionless statement of force balance for a single family of bonds

$$\frac{\alpha}{H_0} \frac{dH_0}{dT} = \int_0^1 N(1-H)R dR, \quad (\text{SI-4})$$

and lets consider the geometry of the attachment process as the adhesion radius slowly grows. The lubrication approximation expressing the height  $H(R)$  as a quadratic function of  $R$  is valid close to the centerline. Far from the center  $R \gg \sqrt{H_0/q}$ , where one may no longer use the simple parabolic approximation for the surface. As the colloid descends, one expects three distinct settling regimes that are different due to a combination of geometry and kinetics. In the first, bonds attach only in the (inner) region close to the center and cause the sphere to descend rapidly. In the second, this rapid descent ends and the adhesion extent now very slowly increases with time as bonds start to attach at heights significantly larger than their rest length but still at radial positions  $R < \sqrt{H_0/q}$ . The final aging process corresponds to bonds attaching near the edge of the sphere where  $\sqrt{H_0/q} < R < 1$ .

Following on from the discussion above, let us decompose the integral into three regions:

$$\int_0^1 dR = \int_0^{R|_{H=1}} dR + \int_{R|_{H=1}}^{R_c} dR + \int_{R_c}^1 dR.$$

Utilizing the parabolic approximation for a sphere  $H = H_0 + \frac{qR^2}{2}$ , we have  $dH = qRdR$  thus allowing the integral to be expressed as

$$\begin{aligned} \frac{\alpha q}{H_0} \frac{dH_0}{dT} &= \int_{H_0}^1 (1-H)dH + \int_1^{1+\frac{1}{\sqrt{2\beta}}} (1-H)dH \\ &+ \int_{1+\frac{1}{\sqrt{2\beta}}}^{H_0+q} N(H_0, R)(1-H)dH \end{aligned} \quad (\text{SI-5})$$

In the first two integrals  $N = 1$ . In the last integral represents we have made explicit  $N$ 's dependence on both  $R$  and  $H_0$  and thus ultimately on time in two senses - the change in  $H_0$  as the sphere settles and more subtly the intrinsic dependence on time that arises as a result of waiting for the binder heads to execute the first passage past the barrier. The first two integrals may be

evaluated to yield

$$\frac{\alpha q}{H_0} \frac{dH_0}{dT} = \frac{1}{2}(1 - H_0)^2 - \frac{1}{4\beta} + \int_{1+\frac{1}{\sqrt{2\beta}}}^{H_0+q} N\{H, T\}(1 - H)dH. \quad (\text{SI-6})$$

That is, the compressed springs in the center behave as an effective nonlinear spring but with an  $R$  independent stiffness. Balancing the first two integrals recovers our expressions for the end of the settling phase,  $H_{0,c}$  and  $R_c$  derived above and described briefly in the main text.

The third integral controls the ultimate dynamics of the aging colloid and in the remainder of this section, we will attempt to approximate its value. To convince ourselves that the final state of the system has the particle making contact with the substrate at infinite time, we evaluate the force imposed on the colloid if all the peripheral bonds were attached (as they would be at infinite time),

$$\int_{1+\frac{1}{\sqrt{2\beta}}}^{H_0+q \approx q} N\{H, T\}(1 - H)dH \approx -q^2.$$

Since  $q \gg 1$ , this force far exceeds the maximum resistive force arising from the compressed springs. The sphere's ultimate fate is to rest on the substrate with the binders effectively holding it in by exerting a net adhesive force. To detach the colloid will involve expending enough energy to break these bonds and overcome this force. This final bound state can be understood as the end result of a series of differential stages. At each stage of the descent, additional bonds must attach to the periphery (at increasingly larger  $R$ ), and then draw the colloid closer to the substrate below until the elastic forces are in approximate balance with the adhesion radius attaining a certain value. The sphere waits (albeit, momentarily) and then executes the next stage once bonds attach again beyond the adhesion region established previously. Of course, we also have the constraint that the sphere can only move as fast as permitted by the drainage of intervening fluid.

Let us evaluate  $\int_{1+\frac{1}{\sqrt{2\beta}}}^{H_0+q \approx q} N\{H, T\}(1 - H)dH$  using the method of steepest descent. The dominant contribution to this integral comes the lower limit. The force an individual bond imposes on the colloid is approximated  $1 - H \approx 1/\sqrt{\beta}$  and the width of the dominant contribution to be  $dH \approx 1/\sqrt{\beta}$ . Estimating this width as the vertical scale over which the attachment rate varies significantly yields

$$\frac{\alpha}{H_0} \frac{dH_0}{dT} \approx -\frac{1}{\beta} \quad (\text{SI-7})$$

This straightforwardly gives us an exponential behavior for the colloid

$$H_0 \approx \exp(-T/\tau_{\text{aging}}),$$

where  $\tau_{\text{aging}} = \alpha\beta q$ . This is however only an intermediate asymptotic regime valid for times that are small enough that no significant attachment occurs beyond  $R > \sqrt{H_0/q}$ . As bonds begin to attach at radial positions  $R > \sqrt{H_0/q}$ , the geometric approximations made to derive the exponential relationship fail and in fact, a decay rate that becomes progressively slower is expected (note the strong decay of the attachment rate with  $R$  indicating progressively larger waiting times for bonds to attach).

To summarize, when a single family of bonds is present and the detachment rate is zero, the initial steep descent is followed by an exponential aging and eventually by an even slower settling regime. Regardless, the divergence in viscous forces ensures that contact cannot happen in finite time, and the zero-detachment rate ensures that the adhesive elastic forces will be perpetually out of balance.

Assuming that the expression for the settling velocity,  $H_0 \approx \exp(-T/\tau_{\text{aging}})$ , extends far enough to allow us to estimate the time for the particle (the lower surface) to descend to a height  $H \approx \mathcal{L}_2 + 1/\sqrt{\beta}$ , whence the second set of adhesive bonds can attach to the particle. Substituting the previous expression into equation (5) we get

$$T^* \sim q\alpha\beta \ln |\mathcal{L}_2 + 1/\sqrt{2\beta}|. \quad (\text{SI-8})$$

shown in Eq. (10) of the paper.

### III. LINEAR VISCOELASTIC RESPONSE TO LATERAL DISPLACEMENTS

Experiments probing the viscoelastic response of settling particles do so by subjecting a constrained, localized particle (held for instance by a laser trap) to oscillatory displacements in the plane parallel to settling direction. We analyze this scenario, assuming that the settling particle executes these lateral oscillatory displacements with an externally controlled frequency and small amplitude  $\Delta(t) = \Delta_o(t)e^{i\omega t}$ . In order that the response corresponds to the linear, quasi-static regime we require that  $\max(\Delta_o) \ll \min(h_o, \ell_1, a)$ ,  $\Delta_o(t)/h_o \ll 1$  (for all  $t$ ) and  $\omega^{-1} \ll \min[h_o(dh_o/dt)^{-1}, n_i(dn_i/dt)^{-1}]$ . Under these conditions, over the time scale over which the response is evaluated, the sphere has not settled significantly and the number of attached bonds

is approximately constant.

An interesting and non-intuitive feature we observe from a linear response analysis is that a particle can be unstable to small transverse displacements. To illustrate this we consider a spring (belonging to family  $i$ ) attached at radial position  $r$  so that the extension is  $h - \ell_i$ . To leading order in  $\Delta_o/h_o$ , the restoring force to an imposed lateral displacement  $\Delta(t)$  is,

$$F_{\text{Elastic}}(t) = -\Delta_o(t) \exp(i\omega t) K_{\text{eff}} \quad (\text{SI-9})$$

where, we have defined an effective lateral compliance (spring constant)

$$K_{\text{eff}} \sim 2\pi \sum_{i=1,2} \int_0^a \mathcal{K}_s n_i(r, t) \left(\frac{h - \ell_i}{h}\right) r dr. \quad (\text{SI-10})$$

Choosing a reference state with zero lateral displacement  $\Delta(t) = 0$  and extension  $h - \ell_i > 0$ , we find from these equations that for pre-extended springs, the restoring force tends to push the sphere back to the reference state. However, for springs that are in a state of compression (in the base state), the imposed elongation results in a restoring force that acts in the direction of the applied elongation - thus providing an effective negative spring constant. A spring that is at its rest length  $h = \ell_i$  does not contribute to any force at this order as the induced extension is second order in  $\Delta(t)$ . Figure (4a) illustrates this feature. Eventually the lateral compliance,  $K_{\text{eff}}$  becomes negative and increases in magnitude until the particle touches the planar substrate. When a finite value of the detachment rate is introduced, as illustrated in figure 4(b), the compliance  $K_{\text{eff}}$  reaches a limiting value at finite time as the sphere reaches a non-zero equilibrium position. This apparent instability arises as a consequence of the linearization. For a spherical particle, the rest height is either zero (when  $k_{\text{off}} = 0$ ) or a value less than the rest height of the families ( $\ell_1$  and  $\ell_2$ ). Binders near the centerline are compressed while those attached far away are extended. As we described earlier, while a binder that is extended when vertical extends even more when displaced laterally and thus exerts a restoring force opposing the displacement, a binder that is compressed in its rest state is in an unstable state with the spring force actually acting in the direction of the displacement. The combination of the two thus yields a height dependent effective compliance - i.e,  $K_{\text{eff}}$  is a function of  $h_0$  and thereby a function of time,  $T$ . Addition of higher order non-linear terms regularizes this instability.

In addition to the frequency independent elastic resistance from the binders, fluid interactions yield both in-phase and out of phase, *frequency dependent* contributions to the linear response

function. The in-phase elastic response is an inertial effect and results from forces proportional to the acceleration of the entrained fluid around the sphere. While no general analytical expression for the forces on a sphere oscillating in a plane parallel to a bounding wall is known, at the level of scaling we can write [1, 2]

$$F_{\text{Viscous}}(t) \sim -A_1 \frac{d\Delta}{dt} + A_2 \frac{d^2\Delta}{dt^2} \left( 1 + \ln \left( \frac{h_o}{a} \right) \right)$$

where as  $h_0/a \rightarrow \infty$ ,

$$A_1 \rightarrow 6\pi\mu a \left( 1 + \frac{a}{\delta(\omega)} \right), \quad \text{and } A_2 \rightarrow 3\pi a^2 \left( 1 + \frac{2}{9} \frac{a}{\delta(\omega)} \right) \left( \frac{2\mu\rho}{\omega} \right)^{1/2}.$$

Here  $\delta(\omega) \equiv \sqrt{\frac{2\mu}{\rho\omega}}$  is the frequency dependent viscous penetration depth (boundary layer) on the sphere surface. The effective elastic response has thus both a frequency independent part due to attached binders and a frequency dependent part due to viscous effects. As the sphere slows down, the elastic contribution dominates the viscous contribution.

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