Size effects in adhesive contacts of viscoelastic media

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Is the maximum force required to detach a rigid sphere from a viscoelastic substrate dependent on the initial value of the contact radius? Experimental and theoretical investigations reported in the literature have given opposite responses.

Here, we try to answer the above question by exploiting a fully deterministic model in which adhesive interactions are described by Lennard-Jones potential and the viscoelastic behaviour with the standard linear solid model.

When the approach and retraction phases are performed under quasi-static conditions, the substrate behaves as an elastic medium and, as expected, the pull-off force $F_{PO}$ (i.e., the maximum tensile force) is found to be independent of the maximum contact radius $a_{\text{max}}$ reached at the end of loading. Size-dependent effects are instead observed (i.e., pull-off force $F_{PO}$ changes with $a_{\text{max}}$) when transient effects occur as the larger the contact area, the greater the size of the bulk volume involved in the dissipation. Results are also discussed in the light of viscoelastic crack Persson’s theory, which is modified to capture size effects related to $a_{\text{max}}$.

I. INTRODUCTION

The estimate of the pull-off force, required to detach two solids in adhesive contact, is of crucial importance in several applications, such as micro-transfer printing [1], tactile sensors [2], biomimetic adhesives [3], soft grippers [4]. In all these technologies, there is a widespread use of soft compliant materials, which often exhibit viscoelasticity and rate-dependent adhesive features, which in turn lead to adhesion hysteresis in loading-unloading cycle [5]. As a result, modeling adhesion between soft matter is a tricky challenge, as shown

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by efforts in recent theoretical studies [6–8].

We lately developed a fully deterministic model for the adhesive contact between a rigid spherical indenter and a viscoelastic substrate [9]. We observed that, when unloading starts from a fully relaxed state of the substrate, the viscoelastic pull-off force $F_{PO}$, i.e., the maximum tensile force, is a monotonic increasing function of the contact line velocity $V_c$ and reaches an asymptotic value at high speeds. If we denote with $F_{PO,0}$ the quasi-static pull-off force (i.e., its value in the elastic limit), at large speeds the ratio $F_{PO}/F_{PO,0}$ should be theoretically equal to $E_\infty/E_0$, being $E_\infty$ and $E_0$ the high and low frequency viscoelastic moduli, respectively. However, $F_{PO}/F_{PO,0}$ is usually lower as a result of finite-size effects. The trend of $F_{PO}$ with $V_c$ is completely different when unloading starts from an unrelaxed state of the material as dissipation involves the bulk volume, and hence it is not confined around the contact line [9].

Based on experimental evidence, researchers have given opposite answers about the dependence of the pull-off force on the point from which unloading starts. For example, Dorogin et al. [10] carried out adhesion tests between a spherical soda-lime glass ball indenter and a PolyDiMethylSiloxane (PDMS) substrate. They used the same value for the approach and retraction speeds of the ball, but they did not specify if any dwell time was waited before unloading. In such conditions, they did not observe a dependence of the pull-off force on the maximum preload and explained that such behaviour is expected when the contact area is simply connected, i.e., when the presence of surface roughness can be neglected.

Similarly, Violano et al. [11] observed an almost constant pull-off force in classical adhesion experiments between a spherical glass indenter and a soft PDMS sample when unloading is performed from fully relaxed state of the material and different preloads.

More recently, Das & Chasiotis [12] performed experiments to study rate-dependent adhesion between polymer nanofibers. To avoid viscoelastic effects during the loading phase, a little crosshead velocity (12 nm/s) was fixed. Retraction was instead performed at greater crosshead velocity (2 µm/s). In such conditions, they also observed $F_{PO}$ to be independent of the preload.

Different results were instead obtained by Baek et al. [13], who performed adhesion experiments between a PDMS block and a spherical glass lens. To minimize viscous dissipation, lens approach was performed in step-by-step movements (with a dwell time of 15 s at the
end of each step). Retraction was performed at fixed speed until the detachment of the lens. They found an increase in the pull-off force with \( a_{\text{max}} \) and, hence, preload. They justified such effect as a consequence of the energy dissipated at the contact interface, as theoretically explained by Maugis & Barquins (MB) [14].

Kroner et al. [15] performed adhesion measurements between PDMS samples and spherical probes. They observed a monotonous increase in the pull-off force with increasing preload, with a maximum asymptotic value reached for higher preloads. Similar results were also obtained in Ref. [16], where adhesion experiments were conducted on polyacrylamide hydrogel.

From a theoretical point of view, the classical Johnson, Kendall & Roberts (JKR) theory predicts a constant pull-off force equal to \( F_{\text{PO},0} = 1.5\pi\Delta\gamma R \), being \( R \) the radius of curvature of the sphere and \( \Delta\gamma \) the adiabatic surface energy. However, JKR theory [17] assumes that contact occurs between elastic media, neglecting viscoelasticity and rate-dependent adhesion.

Attard [18] developed a numerical model for the adhesion of viscoelastic spheres, observing that the pull-off force "will be independent of the maximum applied load. The exception is when the maximum applied load is relatively small".

In a recent work, Jiang et al. [19] developed a finite element model for the viscoelastic adhesive contact between a PDMS stamp and a sphere. In their simulations, unloading starts from a relaxed state of the viscoelastic stamp. They calculated higher pull-off force for increasing preload. Such dependence was found to be more significant for larger unloading velocities.

The detachment of a rigid sphere from a viscoelastic substrate is analogous to the opening of a circular crack. In such case, the effective surface energy \( \Delta\gamma_{\text{eff}} \) required to advance the crack tip by one unit area increases with the crack tip velocity \( V_c \) in the same way of the pull-off force [9]. Two main approaches have been formulated to study viscoelastic cracks, namely the cohesive approach [20, 21] and the energetic one [22, 23], which yield very similar results (see Refs. [8, 9]).

Persson [21] showed that, for system of finite size, \( \Delta\gamma_{\text{eff}} \) does not reach an asymptotic value at high \( V_c \), but it shows a maximum value at intermediate speeds. More recently, Afferrante and Violano [9] and the same Persson [8] have shown that this is true only when unloading starts from an unrelaxed state of the material. In the case of unloading from a
FIG. 1: The problem under investigation: a rigid sphere is pressed into a viscoelastic substrate up to a maximum penetration $\delta_{\text{max}}$, which corresponds to a maximum contact radius $a_{\text{max}}$ and preload $F_{\text{max}}$. The sphere is then detached; both loading and unloading phases are performed at fixed velocity $V = d\delta/dt$.

relaxed state, a different approach than Persson’s one [24] needs to be conceived to capture finite-size effects related to $a_{\text{max}}$.

Moving from this depicted state of the art, in the present paper, we try to clarify how finite-size effects influence the pull-off force and, hence, the effective surface energy $\Delta\gamma_{\text{eff}}$. Specifically, we investigate the influence of the initial contact size $a_{\text{max}}$, from which unloading starts, and propose a modification of Persson’s theory for viscoelastic crack to capture size-effects related to $a_{\text{max}}$.

II. STATEMENT OF THE PROBLEM

The problem under investigation is sketched in Fig. 1: a rigid spherical indenter (with radius of curvature $R$) is pressed into a viscoelastic substrate until a fixed penetration $\delta$ is reached. Different loading histories are considered by increasing the maximum penetration $\delta_{\text{max}}$ (and hence the maximum contact radius $a_{\text{max}}$); the sphere is then detached from the substrate.
FIG. 2: Left: the real (solid line) and imaginary (dashed line) parts of the viscoelastic modulus for a standard linear solid. Right: the standard linear solid used in modelling the viscoelastic properties of the substrate. $E_0$ is the low frequency Young’s modulus, $E_1 = E_\infty - E_0$, where $E_\infty$ is the high frequency Young’s modulus, and $\eta = E_1/\tau$ is the viscosity of the dashpot, being $\tau$ the relaxation time of the material.

The constitutive behaviour of the substrate is modeled with a standard linear solid, whose viscoelastic modulus $E$ is dependent on frequency $\omega$ as shown in Fig. 2. At low frequencies, i.e., in the rubbery region, the material behaves as a soft elastic medium with constant $E(\omega) = E_0$. At high frequencies, i.e., in the glassy region, a stiffer elastic modulus $E(\omega) = E_\infty$ is experienced. At intermediate frequencies, i.e., in the transition region, viscous dissipation occurs and the material behaves as a viscoelastic medium.

A. Numerical solution

To solve the contact problem shown in Fig. 1 we make use of the deterministic finite element (FE) model developed in Ref. [9], at which the reader is referred for the details of the formulation. Here, we briefly recall that interface interactions are modeled by a traction-gap relation based on Lennard-Jones potential law according to Derjaguin’s approximation [25]. Moreover, Maxwell representation (Fig. 2B) of the classical linear standard model is used to describe the viscoelastic behaviour of the substrate

$$E(t) = E_0 + (E_\infty - E_0) \exp(-t/\tau)$$

where $\tau$ is the relaxation time.
Finally, the stress $\sigma$ is calculated according to

$$\sigma = \int_0^t E(t - t') \frac{d\varepsilon}{dt'} dt'$$

(2)

where $\varepsilon$ is the strain and $E(t)$ is the relaxation function.

**B. Modified Persson’s theory**

1. Unloading from relaxed state

In the problem sketched in Fig. 1 the contact mechanical response is concurrently affected by the time-dependent behaviour of the viscoelastic material and finite-size effects. Let us consider a first scenario, where the sphere approaches the substrate at vanishing normal speed $V = d\delta/dt \approx 0$. As a result, quasi-static conditions occur and rate-dependent effects are negligible. In such case, the substrate is in a fully relaxed state at the end of the loading phase. Notice the same condition can be reached by loading at nonzero velocity and waiting a sufficient long dwell time ($t_0 \to \infty$) before unloading [11, 19]. If unloading is then performed at nonzero $V$, the maximum pull-off force $F_{PO(max)}$, which is asymptotically reached at high contact line velocities $V_c = -da/dt$ [9], should be

$$\frac{F_{PO(max)}}{F_{PO,0}} = \frac{E_\infty}{E_0},$$

(3)

being $F_{PO,0}$ the quasi-static pull-off force. However, the ratio $F_{PO(max)}/F_{PO,0}$ is usually lower than that of eq. (3).

In Ref. [26], it is suggested that (3) is true only when adhesion is characterized by short-range adhesive interactions (Tabor parameter $[27] \mu(\omega) = R^{1/3} [\Delta\gamma (1 - \nu^2)/E(\omega)]^{2/3} \gg 5$). However, we suspect that geometric and finite-size effects can also influence the pull-off force and, hence, the effective surface energy $\Delta\gamma_{eff}$ independently of the value of $\mu$.

The detachment of a rigid sphere from a viscoelastic substrate is analogous to the opening of a circular crack [24]; thus, according to Ref. [9]

$$\frac{\Delta\gamma_{eff}}{\Delta\gamma} = \frac{F_{PO}}{F_{PO,0}}.$$  

(4)

Persson & Brener (PB) [23] showed that the surface energy required to advance the crack tip by one unit area is related to the crack tip radius $s(V_c)$ by

$$\frac{\Delta\gamma_{eff}}{\Delta\gamma} = \frac{s}{s_0},$$

(5)
where $s_0$ is the crack tip radius for $V_c \sim 0$ and is related to the stress $\sigma_c$ needed to break atomic bonds through

$$\sigma_c = \frac{K_1}{(2\pi s_0)^{1/2}} = \left( \frac{E_0 \Delta \gamma}{2\pi s_0} \right)^{1/2},$$  

being $K_1$ the stress intensity factor for mode I.

Moreover, from the energy conservation applied to the crack propagation, PB extracted an equation relating the effective surface energy $\Delta \gamma_{\text{eff}}$ (and, hence, the crack tip radius $s$ by eq. (5)) to the viscoelastic modulus $E(\omega)$

$$\Delta \gamma_{\text{eff}} = \Delta \gamma \left[ 1 - \frac{2E_\infty}{\pi} \int_0^{2\pi V_c/s} \frac{F(\omega)}{\omega} \text{Im} \left( \frac{1}{E(\omega)} \right) d\omega \right]^{-1},$$  

where $F(\omega) = [1 - (\omega s/(2\pi V_c))^2]^{1/2}$. Equation (7) leads to the identity (3) at high $V_c$, but it can be used only under the assumptions of: (i) unloading started from a relaxed state of the viscoelastic material, and (ii) system of infinite size.

To take account of the geometry and finite dimension of the contact area, we observe that the problem of detachment of a rigid sphere from a flat substrate, as shown in Fig. 1, is analogous to the problem of a round shaft of radius $a_{\max}$ subjected to a tensile axial load $F$ and with a circumferential crack of initial size $s_0$. In this case, the stress $\sigma_c$ at the tip of the circumferential crack can be corrected according to $\sigma_c = K_1/\left( (2\pi s_0)^{1/2} f(\beta) \right)$, being $f(\beta) = 0.5 \beta^{-1.5} (1 + 0.5 \beta + 0.375 \beta^2 - 0.363 \beta^3 + 0.731 \beta^4)$ and $\beta = (1 - s_0/a_{\max})$ (see Ref. [28]). As a result, one can easily show that (7) modifies in

$$\Delta \gamma_{\text{eff}} = \Delta \gamma \left[ 1 - \frac{2E_\infty}{\pi} \int_0^{2\pi V_c/s} \frac{F(\omega)}{\omega} \text{Im} \left( \frac{1}{E(\omega)} \right) d\omega \right]^{-1},$$  

where the parameter $\alpha$ depends on $s_0$ and $a_{\max}$, and is given by

$$\alpha = \left[ \frac{f(\beta)}{1.1215} \right]^{-2}.$$  

For vanishing $s_0/a_{\max}$, $f(\beta) \to 1.1215$, which is the well-known result for edge cracks. In eq. (9), the constant 1.1215 is hence introduced to obtain the same result of the original eq. (7) in the case of small $s_0/a_{\max}$ (namely, for very large contact radius $a_{\max}$).
When the loading-unloading cycle is performed at fixed nonzero velocity $V = d\delta/dt$ and unloading starts right after the loading phase, the substrate material does not have the time to ‘relax’. Afferrante & Violano [9] showed that the pull-off force reaches a maximum value at intermediate $V_c$ and then decreases by increasing the contact line velocity. This behaviour has been observed also experimentally in Ref. [29] and is related to the finite dimension of the system under investigation [8].

Persson extended his theory of crack’s propagation to the case of finite-sized viscoelastic solids, with application to spheres adhesion [24], by introducing in the integrals of eq. (7) a cut-off frequency $\omega_L$ related to the dimension $L$ of the system

$$\Delta\gamma_{\text{eff}} = \Delta\gamma \left[ 1 - \frac{2E_\infty}{\pi} \int_{\omega_L}^{2\pi V_c/s} \frac{F(\omega)}{\omega} \frac{1}{\omega} \Im \left( \frac{1}{E(\omega)} \right) d\omega \right]^{-1} \tag{10}$$

We have shown, in Ref. [9], that viscous dissipation is no longer confined at the contact edge, but may involve bulk material when unloading starts from an unrelaxed state. In this case, according to Ref. [24], we expect that size effects are governed by the spectrum of frequencies $\omega$ considered in eq. (10). As a result, the parameter $\alpha$ must not be considered here, as its derivation assumes detachment is governed by local effects around the crack tip.

We stress that eq. (10) works only when retraction of the sphere starts from an unrelaxed state of the material and the relaxation modes are not able to totally recover their undeformed state [8]. In this case, it is reasonable to exclude the frequencies $\omega < \omega_L$, being the cut-off dimension $L$ of the order of $a_{\text{max}}$ [24].

III. RESULTS

All results are obtained for $E_\infty/E_0 = 10$, Poisson’s ratio $\nu \approx 0.5$, and are given in terms of dimensionless quantities: $\hat{R} = R/\varepsilon$, $\hat{V} = V\tau/\varepsilon$, $\hat{a} = a/\varepsilon$, $\hat{\delta} = \delta/\varepsilon$, $\hat{F} = F/(1.5\pi\Delta\gamma R)$, being $\tau$ the relaxation time of the viscoelastic material and $\varepsilon$ the range of action of van der Waals forces. All simulations are performed under displacement controlled conditions and for fixed normal velocity $V$ of the spherical indenter.
FIG. 3: The force $\hat{F}$ as a function of the approach $\hat{\delta}$. Loading (black dashed line) is performed at vanishing speed ($\hat{V}_L \approx 0$). Unloading (coloured solid lines) is instead performed at different pulling speeds $\hat{V}_U = 0, 1, 6, 33.333$ and from different maximum penetrations $\hat{\delta}_{\text{max}} = 9.5, 17.7, 25.8, 34$ (corresponding to $\hat{a}_{\text{max}} = 100, 125, 140, 160$). In the inset of each subfigure, the normalized pull-off force $\hat{F}_{\text{PO}} = F_{\text{PO}}/(1.5\pi \Delta \gamma R)$ is plotted in terms of $\hat{\delta}_{\text{max}}$: black and red dashed lines represent JKR "elastic" limit and the upper-bound limit of eq. (3), respectively. Results are given for $\hat{R} = 500$.

A. Unloading from relaxed state

A first set of simulations has been run at vanishing approaching velocity ($V \approx 0$) to avoid time dependent effects during the loading phase and to ensure the detachment process starts from a complete relaxed state of the substrate. Unloading is instead performed at different speeds, starting from different maximum contact penetrations $\delta_{\text{max}}$ (and, hence, different values of $a_{\text{max}}$).

Figure 3 shows the applied force $\hat{F}$ in terms of the penetration $\hat{\delta}$, for different unloading speeds $\hat{V}$ and maximum penetrations $\hat{\delta}_{\text{max}}$. For vanishing unloading velocity (Fig. 3A),
the pull-off force is independent of $\delta_{\text{max}}$, as shown in the inset of the figure. Similarly, the hysteresis loss, which is given by the area between loading-unloading paths, is not affected by the point from which unloading starts. These results are expected as for small $V$ the material response is elastic and falls in the rubbery region. In such case, "elastic" adhesion hysteresis is due to the different values of penetration at which jump-in and jump-off instabilities occur [30]. For unloading velocity $\dot{V} = 1$ (Fig. 3B), viscoelastic effects occur and, although $F_{\text{PO}}$ is almost independent of the maximum penetration, hysteresis loss clearly increases with $\delta_{\text{max}}$. On the other hand, for higher unloading velocities (Figs. 3C-D), both the pull-off force and hysteresis loss grow with $\delta_{\text{max}}$. Interestingly, when $\delta_{\text{max}}$ is increased, pull-off occurs at higher penetrations, which are positive (compressive) at high speeds. In fact, at high $\dot{V}$, the sphere imprint on the substrate is still observed even when the sphere is completely detached [9].

Figure 4 shows the relative increase in viscoelastic pull-off force with respect to the elastic one $F_{\text{PO,0}} = 1.5\pi\Delta\gamma R$. Data are given in terms of the contact line velocity $\dot{V}_{\text{c}}$ calculated at the pull-off and are compared with the theoretical predictions of eq. (8) (coloured solid lines). PB theory for systems of infinite size is plotted with black dashed line. Size-effects related to $a_{\text{max}}$ entail the ratio $F_{\text{PO}}/F_{\text{PO,0}}$ reaches values lower than $E_{\infty}/E_0 = 10$, which is instead approached for infinite system.

Figure 5 shows that $F_{\text{PO(max)}}/F_{\text{PO,0}}$ noticeably reduces when a lower radius $\hat{R} = 50$ is considered. In general, numerical data and theoretical predictions are almost in agreement for $\hat{R} = 500$, while some difference is observed for $\hat{R} = 50$, where the theory underestimates the pull-off force. As discussed in Ref. [7], such differences may be due to a transition of the detachment mode from crack propagation to quasi-uniform bond breaking, which is expected at small scales [31, 32]. This finding is confirmed in Fig. 6 showing the displacement fields. For $\hat{R} = 500$, moving from the time at which the tensile force is maximum ($t_{\text{PO}}$) to the time of final rupture ($t_{\text{rup}}$), crack propagation is clearly the mechanism of debonding; for $\hat{R} = 50$, the displacement field instead moves homogeneously during rupture.

Figure 7 shows the work of separation in terms of the normalized pulling speed $\dot{V}$. Being simulations performed under displacement controlled conditions, $W$ is calculated as $W = \int_{\delta_{\text{snap-off}}}^{\delta_{\text{F=0}}} F(\delta) d\delta$, where $\delta_{\text{snap-off}}$ is the contact penetration at which snap-off occurs and $\delta_{\text{F=0}}$ is the penetration corresponding to zero applied load. Results are normalized with respect to the value calculated in the elastic limit (JKR limit). Unlike the pull-off force $F_{\text{PO}}$ that is
FIG. 4: The relative increase of the pull-off force $F_{PO}/F_{PO(V_c\sim0)} - 1$ in terms of the contact line speed $\dot{V}_c$, being $F_{PO(V_c\sim0)} = 1.5\pi\Delta\gamma R$. Markers refer to FE data; black dashed line refers to PB theory \[23\] for systems of infinite size; coloured solid lines refer to the proposed eq. (8). Results are given for $\dot{R} = 500$ and different $\hat{a}_{\text{max}}$. We assumed $s_0 = 1.5$ nm in the theory.

a monotonically increasing function of $V_c$, $W$ tends to the JKR limit at vanishing velocities and reaches a maximum at intermediate speeds. This may appear counter-intuitive, but the reduction in penetration is small at high pulling velocities $V$ (i.e., when the tensile force takes the highest values) due to a "stick" effect in the initial phase of debonding \[33\] [34]; moreover, such stick effect increases with $\delta_{\text{max}}$. In addition, once the pull-off point is passed, $V_c$ tends to quickly increase especially before snap-off and the assumption of crack-tip velocity slowly changing is no longer satisfied. This is the reason for which the work of separation remains higher than the JKR limit at high $V$ \[4\].
FIG. 5: The relative increase of the pull-off force $F_{PO}/F_{PO}(\hat{V}_c \sim 0) - 1$ in terms of the contact line speed $\hat{V}_c$, being $F_{PO}(\hat{V}_c \sim 0) = 1.5\pi \Delta \gamma R$. Markers refer to FE data; black dashed line refers to PB theory [23] for systems of infinite size; coloured solid lines refer to the proposed eq. (8). Results are given for $\hat{R} = 50$ and $\hat{a}_{\text{max}} = 20$. We assumed $s_0 = 1.5$ nm in the theory.

FIG. 6: Displacement fields when the pull-off force is reached ($t_{PO}$), and at the moment of final rupture ($t_{rup}$) for a pulling velocity $\hat{V}_U = 33.333$ and radii of curvature $\hat{R} = 500$ (A) and $\hat{R} = 50$ (B).
FIG. 7: The work of separation $W$ normalized with respect to JKR value, as a function of the pulling speed $\hat{V}$. Markers refer to FE data; black dashed line refers to the "elastic" quasi-static JKR limit for $E(\omega) = E_0$. Results are given for $\hat{R} = 500$ and different $\hat{a}_{\text{max}}$.

B. Unloading from unrelaxed state

A second set of simulations has been run with approach and retraction performed at the same driving speed $V$ and with zero dwell time ($t_0 = 0$) between the loading and unloading phases. As a result, the approximation of quasi-static loading is no longer valid, and time dependent effects cannot be neglected. Furthermore, being $t_0 = 0$, the stresses in the substrate have no time to relax.

Figures 8A-D show the force $\hat{F}$ in terms of the penetration $\hat{\delta}$ at various loading-unloading speeds $\hat{V} = 1, 6, 33.333, 500$ and different maximum penetrations $\hat{\delta}_{\text{max}} = 9.5, 17.7, 25.8, 34$. During approach, viscous effects lead to a reduction in the effective surface energy, as the system behaves similarly to a closing circular crack [21]. As a result, the loading path is completely different from that observed when $V \approx 0$ (Figs. 3A-D). Moreover, the increase in the pull-off force with $\delta_{\text{max}}$ is more marked already at relatively small velocities. It is interesting to observe what happens at very high loading-unloading rate (Fig. 8D); in this case, the viscoelastic material is excited in its glassy region and behaves as a stiff elastic medium with modulus $E(\omega) \approx E_\infty$. Consequently, the pull-off force is found to be less dependent on $\delta_{\text{max}}$ and closer to the JKR limit $F_{\text{PO,0}} = 1.5\pi\Delta\gamma R$ (which is independent of the value of $E$).

Figures 9A-B shows the relative increase in the viscoelastic pull-off force as a function
FIG. 8: The force $\hat{F}$ as a function of the imposed approach $\hat{\delta}$. Loading (black dashed line) and unloading (coloured solid lines) are performed at the same nonvanishing velocity ($\hat{V}_L = \hat{V}_U = 1, 6, 33.333, 500$). Unloading starts from different maximum penetrations $\hat{\delta}_{\text{max}} = 9.5, 17.7, 25.8, 34$ (corresponding to $\hat{a}_{\text{max}} \sim 100, 125, 140, 160$). In the inset of each subfigure, the normalized pull-off force $\hat{F}_{\text{PO}} = F_{\text{PO}}/(1.5\pi \Delta \gamma R)$ is plotted in terms of $\hat{\delta}_{\text{max}}$; black and red dashed lines represent the JKR "elastic" limit and the upper-bound limit of eq. (3), respectively. Results are given for $\hat{R} = 500$.

of the contact line velocity $V_c$ (calculated at the pull-off). In this case, the maximum value of $F_{\text{PO}}$ does not occur for high $V_c$, but a bell-shape curve is obtained in a double logarithmic representation. Moreover, the peak increases with $a_{\text{max}}$ and occurs at higher $V_c$ when unloading starts from higher contact radius.

When unloading starts from an unrelaxed state of the substrate, we have shown in Ref. [9] that viscous dissipation may involve the bulk material. Therefore, the frequency of excitation can be estimated as $\omega \approx V/a$, being $V$ the normal pulling velocity [35]. At pull-off, we have $V_c/V \approx 20$ when $\hat{R} = 500$ and speeds sufficiently high ($V \geq 6$). On the contrary, for $\hat{R} = 50$
FIG. 9: The relative increase of the pull-off force \( F_{\text{PO}}/F_{\text{PO}(\hat{V}_c \sim 0)} - 1 \) in terms of the contact line velocity \( \hat{V}_c \), being \( F_{\text{PO}(\hat{V}_c \sim 0)} = 1.5\pi\Delta\gamma R \). Markers refer to FE data; black dashed line refers to PB theory [23] for systems of infinite size; coloured solid lines refer to Persson’s theory [24], where in eq. (10) the integrals are calculated between \( \omega_L = \kappa2\pi V_c/a_{\text{max}} \) and \( \omega(s) = 2\pi V_c/s \). We assumed \( s_0 = 1.5 \) nm in the theory. A) Results are given for \( \hat{R} = 500 \) (\( \kappa = 1/20 \)) and different \( a_{\text{max}} \). B) Results are given for \( \hat{R} = 50 \) (\( \kappa = 1/10 \)), and \( \hat{R} = 500 \) (\( \kappa = 1/20 \)).

we find \( V_c/V \approx 10 \) in the limit of high speeds. As in eq. [10], the cut-off frequency is estimated in terms of \( V_c \), we can reasonably assume \( \omega_L = \kappa2\pi V_c/a_{\text{max}} \), with \( \kappa \sim 1/10 \) for \( \hat{R} = 50 \) and \( \kappa \sim 1/20 \) for \( \hat{R} = 500 \). The resulting theoretical predictions are compared with numerical data in Figs. 9A-B, where the solution for systems of infinite size is plotted with black dashed line. We observe that the maximum contact radius \( a_{\text{max}} \) increases with the loading speed \( V \) in numerical simulations but this effect cannot be considered in theoretical calculations. For this reason, in evaluating theoretical curves always the same value of \( a_{\text{max}} \) calculated at \( V \approx 0 \) is considered after we verified it negligibly affects Persson’s curves.

Theory and numerical data are in qualitative agreement even if differences occur in the range of high velocities. Such differences can be explained by observing that the theory returns the effective surface energy “assuming that in the absence of adhesion, there is no elastic energy left in the viscoelastic solid after removing the spherical indenter” [8], while some elastic energy will be necessarily left after unloading. Furthermore, Persson’s theory assumes that the gross of viscous dissipation is localized at the crack tip while, in this case, dissipation also involves bulk material [9]. In addition, we remark that the theory
assumes steady-state crack propagation, while in our simulations $V_c$ is not constant during detachment as shown in Fig. 10 where the dependence of $\hat{V}_c$ on the contact radius $\hat{a}$ is plotted for a pulling speed $\hat{V} = 6$. The contact line velocity $\hat{V}_c$ varies widely (about two orders of magnitude) moving from $\hat{a}_{\text{max}}$ to snap-off, and the pull-off point is not reached under steady-state conditions.

Finally, Fig. 11 shows the work of separation in terms of the pulling velocity for different initial values of the contact radius. $W$ increases with $a_{\text{max}}$ except at low and high speeds where the viscoelastic substrate responds elastically with $E(\omega) = E_0$ at vanishing speeds, and $E(\omega) = E_\infty$ at very high $V$. In such limits, the JKR values of $W$ are recovered.

IV. CONCLUSIONS

Size-dependent effects in the adhesion of soft materials find partial explanation in the scientific literature, where the correlation between size and rate effects is often neglected. For this reason, in this work, we try to shed some light on this problem through the investigation of the adhesive contact between a rigid sphere and a viscoelastic substrate, by exploiting a recent FE model developed in Ref. [9].

We have performed various simulations under different loading and unloading conditions. When unloading starts from a fully relaxed state of the viscoelastic material, the pull-off force (and hence the effective surface energy) is a monotonic increasing function of the contact
FIG. 11: The normalized work of separation $\hat{W}$ in terms of the pulling speed $\hat{V}$. Markers refer to FE data; black dashed lines refer to the "elastic" quasi-static JKR limit for $E(\omega) = E_0$ and $E(\omega) = E_\infty$. Results are given for $\hat{R} = 500$ and different $\hat{a}_{\text{max}}$.

line velocity $V_c$. For systems of infinite size, Persson & Brener (PB) [23] theory predicts $F_{\text{PO}(\text{max})}/F_{\text{PO},0} = E_\infty/E_0$ at high $V_c$, while numerical calculations show that the asymptotic maximum value $F_{\text{PO}(\text{max})}$ of the pull-off force is affected by the finite dimension of the contact radius. For this reason, we suggest introducing a corrective factor $\alpha(s_0, a_{\text{max}})$ in PB theory which takes into account geometric effects related to the system under investigation (and, in particular, the finite value of the contact radius $a_{\text{max}}$ reached at the end of loading). A good agreement is found between theory and numerical data, although some differences are observed for the smaller curvature radii of the sphere, as a transition of the detachment mode from crack propagation to quasi-uniform bond-breaking may occur at small scales.

When loading-unloading are performed at the same nonvanishing driving speed $V$ (and without waiting time between approach and retraction), the pull-off force $F_{\text{PO}}$ shows a peak at intermediate $V_c$. Such peak increases with $a_{\text{max}}$ and moves towards higher $V_c$ when unloading starts from a higher initial contact radius. At very high $V_c$, the substrate behaves again elastically with an elastic modulus $E_\infty$. Also, Persson’s theory [8, 24] agrees with FE calculations but some quantitative differences can be observed at the highest speeds as a result of the simplifying assumptions included in the theoretical model.
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